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Assessment of integrity of three dispersants and their toxicity to a Brackishwater Cichlid, *Sarotherodon melanotheron* (Cichlidae)

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ABSTRACT: Key physical characteristics of three dispersants: Corexit 9527, NalcoD4106 and Goldcrew were studied to determine their integrity and toxicity to a brackishwater fish *Sarotherodon melanotheron*. The results showed that with regards to the physical properties, Corexit 9527 and to a large extent Goldcrew maintained their integrity while NalcoD4106 deteriorated. Observations of the 96h LC_{50} static bioassay showed that the toxicity of the dispersants to the fish in an increasing order is Corexit 9527 < Goldcrew < NalcoD4106. Crude oil – dispersant mixtures involving either Corexit 9527 or Goldcrew were less toxic than crude oil alone. On the other hand, NalcoD4106 exhibited higher toxicity than crude oil either as dispersant alone or as dispersant – crude oil mixture.

Key words: Bioassay; Dispersant; Crude Oil (Petroleum); Integrity; LC_{50}; Toxicity Factor.

Introduction

According to the United States coast guard emergency response notification system (ERNS), Crude oil is one of the most commonly spilled petroleum products in the world both by number of notification and by volume (Irwin *et al*., 1997). Crude oil vary considerably in their toxicity and the sensitivity of fish to petroleum products varies according to species (IPIECA, 2001). The impacts to fish are primarily to the eggs, larvae and early juvenile with considerable effect on the adult (Irwin *et al*., 1997). Spills involving large volumes of oil have been reported such as the Amoco Cadiz, Torrey Canyon, Tenneco, The West Falmouth spill, Funiwa -5- oil blow-out (Simpson, 1968; Law, 1981; Ekekwe, 1981). Regardless of any action taken after a major oil spill has occurred in the marine environment, both the marine and possibly coastal environments will suffer environmental damages.

The consequences of oil spills on the biological and physical processes in aquatic environment have been well established (Nelson – Smith, 1968; Baker and Crapp, 1974 and Laws, 1981). The effect of marine oil pollution on aquatic organisms, mangrove and its community are very diverse and complex. To advert these deleterious effects of oil spills, pollution control measures have been taken internationally and nationally to protect the aquatic environment. Such measures include mechanical removal and recovery of spilled oil, use of chemical dispersants and micro-organisms (Engdahl, 1981).

Measures have been taken globally in recent times to protect the aquatic environment by ensuring that spilled oil is removed from the environment as quickly as possible, and one of such recovery measures is by the use of chemical dispersants. Chemical dispersants are mixtures that contain "surface-active chemicals" (SURFACTANTS) and SOLVENTS. The surfactants actually cause the oil to "disperse" into tiny droplets that remain suspended in the water column. The droplets are dispersed into the water column by natural processes such as water movements, currents and atmospheric phenomenon. Although dispersants have been found effective in oil clean-up operations, their use as dispersants alone or as dispersants-oil mixture may be toxic to organisms.

This study intends to assess the integrity of the dispersants commonly used in Nigeria for oil clean-up and to determine their toxicity to aquatic animals using a brackishwater fish *Sarotherodon melannotheron* as an indicator.

Materials and Methods

Three dispersants namely Corexit 9527, NalcoD4106 and Gldcrew as well as Forcados blend crude oil were used for this study. The specimen on which the study was conducted is *Sarotherodon melanotheron*, a brakishwater fish, which was obtained from the African regional aquaculture center (ARAC) in Port Harcourt, Nigeria. The stock population of the specimens was in a 30 liters holding tank, aerated by air pumps with diffusers, and acclimatization of the specimens was for ten days. The test vessels were made of glass with a working capacity of 2.5 litres, and agitation was by stirring intermittently with a glass rod. Healthy specimens, each of about the same weight (0.68-0.72kg) were used. The laboratory ambient temperature was 27.5±2°C; relative humidity was 80±3%. The dissolved oxygen concentration ranged from 5.0 to 6.2mg/l in the tank, temperature ranged from 28°C to 30°C, pH ranged from 7.2 to 7.5 while salinity concentration ranged from 19.0% to 20.1%.

Semi-static bioassay procedure as described by Reish and Oshida (1974) and as recommended by department of Petroleum Resources (DPR, 1989) guidelines for the determination of acute toxicity of dispersants under Nigerian environmental condition was carried out. The physical and chemical properties of the dispersants were determined employing methods described in American Society for Testing and Materials (ASTM, 1994).

Bioassay data for survival were statistically analyzed to determine percentage mortality, these were plotted against concentration on probit graph paper (Finney, 1971) and values of LC_{50} were determined from the line of best fit. The 95% confidence limits were computed to establish if the difference in the LC_{50} values obtained were statistically significant.

Results

A summary of the physical and chemical properties of the dispersants is shown in Table 1. The data obtained from the bioassays showing the percentage mortalities computed from the number of death at 96hrs are given in Figure 1a-b. Analyses for LC_{50} values obtained with dosage versus percentage mortality of *S. melanotheron* are presented in Table 2. The result showed that the LC_{50} value for Corexit 9527 was 11.0mgl^{-1} while value obtained for NalcoD4106 was 4.0mgl^{-1} and that of Goldcrew was 8.0mgl^{-1}. From these results, it can be seen that the toxicity of the dispersants in an increasing order was as follows: Corexit 9527 < Goldcrew < NalcoD4106. Table 3 shows the relative potency of the dispersants based on 96hr LC_{50} values. The result shows that NalcoD4106 was twice as potent as Corexit 9527 and 1.3 times as potent as Goldcrew when tested against *S. melanotheron.*

The LC_{50} values of the crude oil were 6.0mgl^{-1} when tested against *S. melanotheron*. This showed that the crude oil was 2 to 3 times as toxic as Corexit 9527, 0.67 to 1.5 times as toxic as NalcoD4106 and 1.3 times more than Goldcrew (Table 4). The results of the determination of LC_{50} for the dispersants – crude oil mixtures against the fish showed that Corexit 9527 – crude oil mixture had a value of 26.0mgl^{-1}, NalcoD4106 – crude oil mixture gave LC_{50} value of 21mgl^{-1} while Goldcrew – crude oil mixture produced LC_{50} value of 16mgl^{-1} (Table 2).

Table 1: A summary of the physical properties of three dispersants

Name and Year of Delivery	pH	Specific gravity	Viscosity at 280C (Cst)	SOLUBILITY				% water content	Evaporation rate mg/g/cm2/h	Conduct-tivity us/cm	Boiling point °C	Freezing point °C	Particulate formation	Emulsion formation	Opacity	Appearance and Colour
				Fresh water	Brackish water	Sea water	Hydro-carbon									
Corexit 9527	7.1	1.02	62+++	Sol.		Slight Sol.	Sol.	18	'1.0	1264	73	-43	-	+++	+	Slightly amber liquid
NalcoD4106 (1993)	7.1	1.12	19+	Sol.		Sol.	Sol.	72	2	94100	67	-13	+++	+	++	
Gold crew	7.2	1.01	46++	Sol.		Slight Sol.	Sol.	32	1.2	10130	69	-32	-	++	+	

- None
+ Slight
++ Moderate
+++ Extensive

Table 2: Static Bioassays showing 96hr LC_{50} values (mg/l) of dispersant, crude oil and crude oil – dispersant mixtures tested against *Sarotherodon melanotheron*.

DISPERSANT + WATER	CRUDE OIL + WATER	DISPERSANT + OIL + WATER
Corexit 9527	Crude oil	Corexit 9527 + Crude oil
11.0	6	26
(7.6-15.8)	(4.7-7.6)	(15.4-30.6)
NalcoD4106		NalcoD4106 + Crude oil
4.0		21
(1.7-9.5)		(17.8-29.1)
Goldcrew		Goldcrew + Crude oil
8.0		16
(5.7-11.1)		(3.4-14.7)

Figures in parentheses indicates range of 95% confidence limit.

Table 3: Relative potencies (toxicity factors**) of dispersants, crude oil, crude oil-dispersant mixtures tested on *S. melanotheron* in 96h static bioassays.

TEST SOLUTIONS	TOXICITY FACTORS
i **Dispersant – crude oil**	
Corexit 9527/Crude oil	2
NalcoD4106/Crude oil	0.67
Goldcrew/Crude oil	1.3
ii. **Crude oil – Dispersant mixtures**	
Corexit – Crude oil – Crude oil	4.3
Nalco – Crude oil – Crude oil	3.5
Goldcrew – Crude oil – Crude oil	2.7
iii. **Dispersant – Dispersant**	
Corexit 9527/NalcoD4106	2.0
Corexit 9527/Goldcrew	1.5
Goldcrew/NalcoD4106	1.3

**Toxicity factor = A ratio relative potency based on 96h LC_{50} values.

Discussion

The integrity of a dispersant is determined by the stability of its physical properties such as specific gravity, viscosity, pH, solubility, evaporation rate, opacity and the ability to form emulsions, National Research Council (NRC, 1989). The factors that are most likely to influence whether a chemical dispersants will be an effective response are not those associated with the integrity of the dispersant or the dose rate, instead, it will be issues such as the type of oil spilled, sensitive resources at risk, priorities for protection and whether or not a particular country has a clear policy and plan in place for the use of dispersants (IPIECA, 2001).

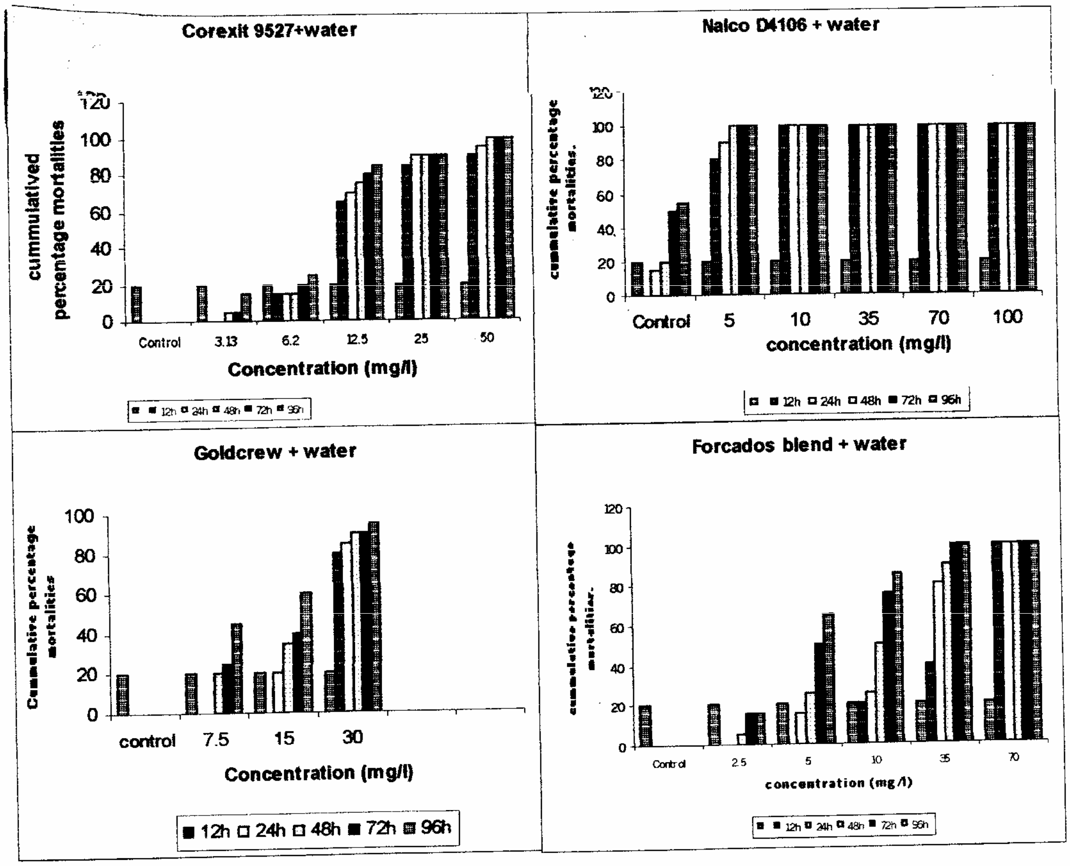

Fig. 1a: Cumulative (%) mortalities of *Sarotherodon melanotheron* exposed for 96 hours in Semi-static bioassays to varying concentration of test chemical in Brackish water

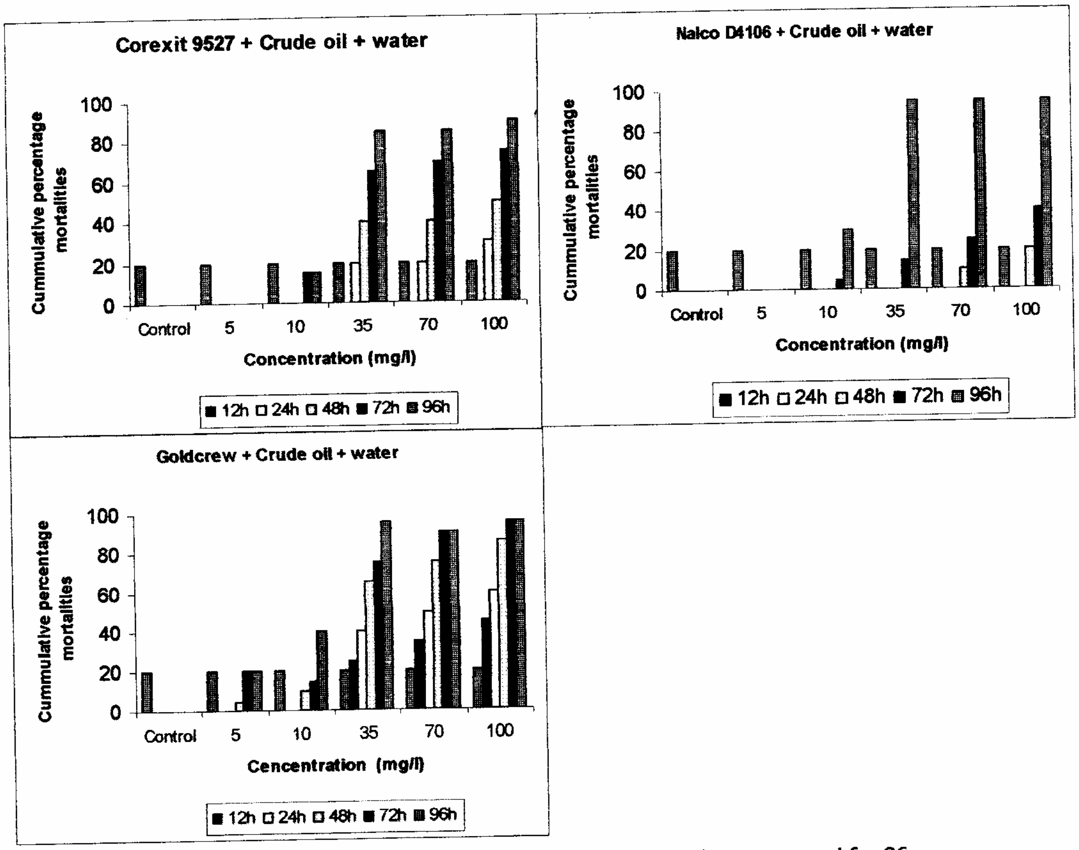

Fig. 1b: Cumulative (%) mortalities of *Sarotherodon melanotheron* exposed for 96 hours in Semi-static bioassays to varying concentrations of test chemicals and forcados blend crude oil in brackish water.

The results of this study shows that the properties of Corexit 9527 and Goldcrew appear to have maintained their integrity, as there was no significant difference in characteristics between the findings of this study and those given by the manufacturers. NalcoD4106 however, had values that deviated from those given by the manufacturers such as higher specific gravity, decrease in particulate formation and elevated conductivity. This deviation indicates some measure of instability in stired NalcoD4106. However, this may also be attributed to the storage containers, for instance, Corexit 9527 and Goldcrew were stored in plastic drums while NalcoD4106 was stored in metal containers. There is therefore the possibility of NalcoD4106 reacting with the metal container resulting in higher toxicity.

The results also showed differential toxicity of the chemicals, NalcoD4106 showed a tendency to increase its toxicity in storage with regard to varying toxicities to *S. melanotheron* more than Corexit 9527 and Goldcrew. Differences in toxicity of dispersants have been well documented by earlier workers (Beynon, 1970; Laws, 1981). The toxicities of the dispersants in an ascending order were as follows: Corexit 9527 < Goldcrew < NalcoD4106. The relative potency of the dispersants based on LC_{50} values obtained showed that NalcoD4106 was twice as toxic as Corexit 9527 and 1.3 times as potent as Goldcrew when tested against the fish specimen.

The LC_{50} values obtained for the crude oil revealed that the crude oil was 2 to 3 times as toxic as Corexit 9527, 0.67 as NalcoD4106 and 1.3 times as Goldcrew. Nelson-Smith (1968), Baker and Crapp (1974) and Laws (1981) had earlier recorded higher toxicity of crude oil over dispersants.

The results obtained from the dispersants-crude oil mixtures test against *S. melanotheron* revealed a lower toxicity of the resulting suspension compared to the toxicity level of the dispersantalone or of crude oil alone. Corexit 9527 – crude oil mixture was 4.3 times less toxic than crude oil alone; NalcoD4106 – crude oil mixture was 3.5 times while Goldcrew – crude oil mixture was 2.7 times less toxic when tested against *S. melanotheron*.

The significance of the 96hr LC_{50} values obtained in this study using crude oil alone, individual dispersants and crude oil – dispersant mixture lies on the fact that when an oil spill occurs in the sea, the crude oil forms a film on the surface of the sea water where marine organisms come in contact with it. On application of a dispersant, the marine organisms become exposed to the crude oil – dispersant mixture rather than a suspension or solution of the dispersant alone (Norton *et al*., 1978). Economic factors will invariably play an important part in the decision of whether or not to use chemical dispersant, a tourist beach may generate considerable income for the local economy and so be a priority area for protection. Knowledge of the relative toxicities of the crude oil alone, the dispersant and crude oil – dispersant mixture in addition to other prevailing factors will enable a rational decision on the desirability or otherwise to use a particular dispersant on the oil spill.

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