The comparative Toxicities of two petroleum Products, Automotive Gas Oil, AGO and Premium Motor Spirit, PMS on fresh and Brackish Water Habitat

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Abstract
The comparative toxicities of two petroleum products, Automotive Gas Oil (AGO) and Premium Motor Spirit (PMS), were examined by exposing two species of shrimp: freshwater shrimp Desmoscaris trispinosa and brackish water shrimp Palaemonetes africanus, to acute concentrations (0.05, 0.1, 1.0, 10.0, and 100 mg/L) of these toxicants for 96 hours. The toxicity was examined in artificially contaminated environmental systems, and the median lethal concentration (LC50) was estimated using the Finney Probity method of analysis. The acute toxicity evaluation yielded 96-hour LC50 values for AGO of 0.330 mg/L for freshwater shrimp and 1.986 mg/L for brackish water shrimp, compared to 0.485 mg/L and 2.919 mg/L for PMS in freshwater and brackish water habitats, respectively. These results indicated that AGO was more toxic than PMS, and both petroleum products were more toxic to the freshwater shrimp than to the brackish water shrimp. However, the observed mean LC50 values were not significantly different at levels of $p < 0.01$. The findings suggest that petroleum products pose potential risks to the fauna in the shoreline and benthic sediments of the Niger Delta ecological zone. This is important because attention is often focused on visible surface spills of petroleum, while the dissolved aromatic hydrocarbons, which are more bioavailable and potentially toxic to marine organisms, are overlooked.

Keywords: *Petroleum Products, Heavy Metals, Dissolved Oxygen, Cations, Anions*

Introduction

The discharge of toxic pollutants into fresh and marine environments presents risks to the biota, in particular, to sessile, bottom-dwelling organisms, unless contaminant concentrations remain below certain tolerable concentrations (Dickson et al., 1987).

The refined petroleum products Automotive Gas Oil (AGO) (diesel) and Premium Motor Spirit (PMS), often known as petrol or gasoline, both include hydrocarbon compounds. The lighter fraction, Premium Motor Spirit, ranged from 5 to 12 carbon chains, whereas Automated Gas Oil ranged from 16 to 18 carbon atom chains. Premium Motor Spirit is more flammable than automated gas oil, yet both are flammable. These volatile liquids are used as solvents for paints and greases as well as fuel for cars, trucks, generators, home heating and cooking, flying in jet aircraft, and other devices (Jumoke, 1999; Omofonmwan et al., 2009). Due to the rise in oil pollution, which can be attributed to spills, leaks from corroded pipes, vandalism, etc., there is a

growing interest in the consequences of crude oil and its fractions. Most research on the impacts of oil pollution in the aquatic environment, according to Tijjani et al. (2012), only looks at the effects of full crude or refined fractions. The majority of these investigations (Nwilo et al., 2005; Nwachukwu et al., 2014) are conducted on fish, which may quickly travel from the polluted area to free zones. Crude oil and its byproducts enter the aquatic ecosystem and seriously harm the aquatic ecology in a number of ways. The availability of oxygen to aquatic flora and fauna can be restricted in one way (Nwilo et al., 2005), and the biochemical and physiological processes of the organism in touch can also be negatively impacted (Temara et al., 1999; Dabestani et al., 1999). Additionally, according to Clemens et al. (2009), there are no generic standards for the toxicities of the different crude fractions, so it is necessary to figure out the concentrations at which they become harmful to the environment as well as to compare the toxicities of the different parts of the crude so that appropriate standards and legislation can be put in place. It is important to determine the possible toxicity of crude fractions and dose-response relationships with sensitive species, particularly with species that move extremely slowly, like crabs and molluscs. The destiny and impacts of these chemicals in marine environments are determined by the chemical and physical characteristics of crude oils or refined products. The lightest oils may be acutely harmful to people, fish, and other biota and spread quickly on solid or liquid surfaces. The biodegradation and weathering processes are relatively sluggish, and the dispersion may be weak.

Materials and method

Semi-Static Bioassay Techniques:

Acute toxicity tests were carried out with aquatic organisms by exposing them (the test organisms) to test solutions containing various concentrations of the test sample using the semi-static agitation test procedure as recommended by the Department of Petroleum Resources (DPR, 2002).

Sampling and Acclimatisation of Test Organisms:

Freshwater shrimp, *Desmoscaris trispinosa,* were collected from Odiereka Swamp off Orashi freshwater swamp, Ogba-Egbema, and Ndoni L.G.A. in River State. The juvenile shrimps were caught using nets at spring tide and were immediately transferred into containers containing the habitat water (APHA, 2012). Juveniles were collected because of their small size and sensitivity to toxicants.

Brackish-water juvenile shrimp (*Palaemonetes Africanus)* were collected from the brackish water at Aboturu Creek off Bonny River, Ogu-Ogboro L.G.A. of River State. The shrimp were collected with the aid of sieves of an appropriate mesh size during the spring tide. They were transferred into containers containing the habitat water (APHA, 2012).

All test organisms were first acclimatised for ten days at room temperature ($28 \pm 2\ ^{o}C$). They were acclimatised in dark glass tanks into which air (oxygen) was continuously bubbled through an aerator. They were also fed fish feed obtained from the Institute of Fisheries at Aluu, near the University of Port Harcourt, during the period of analysis. The water in the acclimatisation units was replaced daily with fresh water from the organism's habitat. A controlled lighting system with 12 hours of light and 12 hours of darkness was employed.

The refined petroleum products were obtained from the Total Petrol Station in Port Harcourt, Rivers State.

Selection of Test Organisms:

Twenty test organisms of fairly equal size were randomly caught with a hand net from acclimatisation tanks and carefully transferred into the test vessel. The organisms were not touched with hands during the selection so as to avoid stress due to handling. Only healthy and active test organisms were selected.

Test Medium:

Five different concentrations of the test sample (0.05 mg/l, 0.1 mg/l, 1.0 mg/l, 10.0 mg/l, and 100 mg/l) were prepared using the habitat water of the particular organism as a diluent.

Twenty test organisms were used in each concentration. Healthy, active test organisms were carefully introduced into bioassay vessels representing different concentrations. Controls containing dilution water and twenty test organisms were prepared without the toxicant, and this served as the control. Each of the test concentrations was labelled appropriately. After each day, the media were replaced with fresh ones. Dead organisms were also removed at the end of each exposure period. This was done to avoid contamination of live organisms by bacteria from dead, decaying organisms. Mortality was recorded at 4, 8, 24, 48, 72, and 96-hour exposure periods (Finney, 1978; Sprague, 1973).

Range Finding Test:

A test was carried out to establish a preliminary working range by obtaining the least concentration that gives no effect and the minimum concentration that gives 100% death. The test design incorporated multiple, widely spaced concentrations with single replicates. Exposure times were 4 hours, 8 hours, 24 hours, 48 hours, and 96 hours.

Preparation of water-soluble fractions (WSFs) of AGO and PMS

Water-soluble fractions of AGO and PMS were prepared using an oil-to-water ratio of 1:3. 500 ml of AGO oil was mixed with 1500 ml of water samples (fresh water), and the mixture was stirred using a magnetic stirrer for 24 hours at room temperature. After stirring, the mixture was allowed to stand for a minimum of 3 hours to obtain a clear interphase between oil and water. The oil was decanted, and the mixture was then poured into a glass stopper-separating funnel and allowed to stand overnight. Pure and clear WSF obtained at the lower part of the funnel was syphoned into capped bottles to make the stock (100% WSF). The procedure was repeated using PMS until sufficient quantities of WSFs of AGO and PMS were obtained and stored in dark brown screw-cap bottles prior to analysis. The process was repeated using brackish water.

LC_{50} Determination

By means of a table, the numbers of dead shrimp in each group were recorded against the time of their death, according to Sprague (1973).

The median lethal concentration (LC_{50}) was calculated using this data of the water-soluble fraction (WSF) on Desmoscaris *trispinosa* and *Palaemonetes africanus* with the Probit method of Dede et al. (2001).

Physico-Chemical Analysis:

Standard analytical procedures were used in the determination of selected physical, chemical, and biological water quality parameters of the samples. Selected physicochemical analyses such as pH, temperature, turbidity, conductivity, total suspended solids (TSS), nitrates, total hardness, magnesium, calcium, dissolved CO_2, etc. were carried out.

Determination of the Physical Properties of Water Soluble Fractions (WSFs)

pH was determined using an EIL Model 720pH meter. Electrical Conductivity (EC) was measured using the portable conductivity meter (Hanna) and the value was expressed in 4 µs/cm

Biochemical oxygen demand and dissolved oxygen were measured using the modified oxygen depletion and Winkler's method (APHA, 2012)

Determination of Electrical conductivity (EC)

Electrical Conductivity (EC) was measured using the portable conductivity metre (Hanna), and the value was expressed in 4 µs/cm. EC was measured using a standard solution of potassium chloride of known conductivity (0.01 NKCI, 745.6 mg in 1.0 L deionized water = 1413 µohms/cm) in accordance with APHA (2012).

Determination of Dissolved Oxygen (DO) and Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand and dissolved oxygen were measured using modified oxygen depletion and Winkler's method (APHA, 2012).

Determination of Chemical Oxygen Demand (COD)

This is a measure of the oxygen proportion of the untreated matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. The COD was determined according to the method described in ALPHA (2012).

Determination of Chemical Properties of WSFs

Determination of Salinity:

The salinity of the water sample was measured in the laboratory as described in the Horiba Instruction Manual (HIM, 1991). About 20 ml of water was dispensed into a beaker, and the salinity was read by immersion of the probe after standardisation for about 3 minutes.

Determination of Hardness:

Total hardness in water was determined in accordance with (APHA, 2012).

Determination of Sulphate

Sulphate was determined by the turbidimetric method. The sample was reacted with barium ions in the presence of sodium chloride and a hydrochloric acid solution containing glycerol and ethyl alcohol. The colloidal barium sulphate formed was measured at 420nm using a UV/visible spectrophotometer (APHA, 2012).

Determination of Nitrate

Two millilitres of brine reagent were added to 10 ml of sample in a 25 ml volumetric flask, and 10 ml of H_2SO_4 concentration was rapidly added. The mixture was allowed to stand for 20 minutes and made up to mark with distilled water before measurement at 470nm with a UV/visible spectrophotometer (ASTM, 2010).

Determination of Ammonium Nitrogen

6 ml of potassium sodium tartrate, 2 ml of alkaline sodium phenate solution, and 2 ml of sodium hypochlorite solution were added to 10 ml of the sample in a 25 ml volumetric flask. The mixture was made up of distilled water, and the absorbance value was set at 630nm on a UV/Visible spectrophotometer (ASTM, 2010).

Determination of Phosphate

1 ml of sample was pipetted into 10 ml of 0.7M HCl and stirred briefly. 1 ml of the molybdate reagent was then added to the vial, and the contents were stirred for two to three minutes. Exactly 5 ml of 1-butyl acetate was then added, and the contents were stirred thoroughly into an emulsion

for 2 to 3 minutes. The phases were then allowed to separate, and as much of the organic as possible was transferred to a second vial containing 5 ml of 0.85M HCl. The contents of this vial were then stirred for 1 to 2 minutes, and the phases separated for 3 minutes. The Organic was then transferred to a 1-cm spectrophotometer cell, and the absorbance was measured against a reagent blank at 310 nm (ASTM, 2012).

Determination of Calcium and Magnesium

5 ml of buffer solution and 0.5 mL of KCN and hydroxylamine hydrochloride solution were added to 25 mL of water-soluble fraction (WSF) in a 250 mL conical flask. 2 drops of Erichrome Black T indicator solution were added to the mixture and titrated over a white surface with standard 0.004M EDTA. Calcium and Magnesium were determined by flame photometry (ASTM, 2010).

RESULTS

Toxicants in fresh and brackish water habitat

TABLE: 1

LC_{50} Evaluation of AGO and PMS on Brackish Water Crustacean *Palemonetes Africanus* (4 Hours)

Toxicant	Conc. (mg/L)	Number surviving	Percentage (%) surviving	Percentage (%) mortality
AGO	0.05 0.10 1.00 10.00 100.00	20 20 19 18 17	100 100 95 90 85	0 0 5 10 15
PMS	0.05 0.10 1.00 10.00 100.00	20 20 20 20 19	100 100 100 100 95	0 0 0 0 5

TABLE: 2

LC_{50} Evaluation of AGO and PMS on Brackish Water Crustacean *Palemonetes Africanus* (8 Hours)

Toxicant	Conc. (mg/L)	Number surviving	Percentage (%) surviving	Percentage (%) mortality
AGO	0.05 0.10 1.00 10.00 100.00	20 19 18 17 17	100 100 90 85 85	0 5 10 15 15
PMS	0.05 0.10 1.00	20 20 19	100 100 95	0 0 5

	10.00 100.00	19 19	95 95	5 5

TABLE: 3
LC_{50} Evaluation of AGO and PMS on Brackish Water Crustacean *Palemonetes Africanus* (24Hours)

Toxicant	Conc. (mg/L)	Number surviving	Percentage (%) surviving	Percentage (%) mortality
AGO	0.05 0.10 1.00 10.00 100.00	20 16 15 10 6	100 80 75 50 30	0 20 25 50 70
PMS	0.05 0.10 1.00 10.00 100.00	20 19 18 17 15	100 95 90 85 75	0 5 10 15 25

TABLE 4
LC_{50} Evaluation of AGO and PMS on Brackish Water Crustacean *Palemonetes Africanus* (48Hours)

Toxicant	Conc. (mg/L)	Number surviving	Percentage (%) surviving	Percentage (%) mortality
AGO	0.05 0.10 1.00 10.00 100.00	20 14 11 9 4	100 70 55 45 20	0 30 45 55 80
PMS	0.05 0.10 1.00 10.00 100.00	20 18 17 16 15	100 90 85 80 75	0 10 15 20 25

TABLE 5
LC_{50} Evaluation of AGO and PMS on Brackish Water Crustacean *Palemonetes Africanus* (72Hours)

Toxicant	Conc. (mg/L)	Number surviving	Percentage (%) surviving	Percentage (%) mortality
AGO	0.05	19	95	5
	0.10	11	55	45
	1.00	9	45	55
	10.00	6	30	70
	100.00	2	10	90
PMS	0.05	20	100	0
	0.10	17	85	15
	1.00	16	80	20
	10.00	15	75	25
	100.00	14	70	30

TABLE 6
LC_{50} Evaluation of AGO and PMS on Brackish Water Crustacean *Palemonetes Africanus* (96Hours)

Toxicant	Conc. (mg/L)	Number surviving	Percentage (%) surviving	Percentage (%) mortality
AGO	0.05	17	85	15
	0.10	8	40	60
	1.00	6	30	70
	10.00	2	10	90
	100.00	0	0	100
PMS	0.05	19	95	5
	0.10	15	75	25
	1.00	12	60	40
	10.00	10	50	50
	100.00	8	40	60

TABLE 7
LC_{50} Evaluation of AGO and PMS on Fresh Water Crustacean *Desmoscaris Trispinosa* (4 Hours)

Toxicant	Conc. (mg/L)	Number surviving	Percentage (%) surviving	Percentage (%) mortality
AGO	0.05	20	100	0
	0.10	20	100	0
	1.00	19	95	5
	10.00	19	95	5
	100.00	18	90	10
PMS	0.05	20	100	0

	0.10	20	100	0
	1.00	20	100	0
	10.00	20	100	0
	100.00	19	95	5

TABLE 8
LC_{50} Evaluation of AGO and PMS on Fresh Water Crustacean *Desmoscaris Trispinosa* (8 Hours)

Toxicant	Conc. (mg/L)	Number surviving	Percentage (%) surviving	Percentage (%) mortality
AGO	0.05	20	100	0
	0.10	20	100	0
	1.00	18	90	10
	10.00	18	90	10
	100.00	17	85	15
PMS	0.05	20	100	0
	0.10	20	100	0
	1.00	19	95	5
	10.00	19	95	5
	100.00	19	95	5

TABLE 9
LC_{50} Evaluation of AGO and PMS on Fresh Water Crustacean *Desmoscaris Trispinosa* (24 Hours)

Toxicant	Conc. (mg/L)	Number surviving	Percentage (%) surviving	Percentage (%) mortality
AGO	0.05	20	100	0
	0.10	18	90	10
	1.00	16	80	20
	10.00	12	60	40
	100.00	8	40	60
PMS	0.05	20	100	0
	0.10	19	95	5
	1.00	19	95	5
	10.00	18	90	10
	100.00	16	80	20

TABLE 10
LC_{50} Evaluation of AGO and PMS on Fresh Water Crustacean *Desmoscaris Trispinosa* (48 Hours)

Toxicant	Conc. (mg/L)	Number surviving	Percentage (%) surviving	Percentage (%) mortality
AGO	0.05	20	100	0
	0.10	16	90	10
	1.00	13	80	20
	10.00	11	60	40

	100.00	5	40	60
PMS	0.05	20	100	0
	0.10	19	95	5
	1.00	18	90	5
	10.00	17	85	15
	100.00	15	75	25

TABLE 11
LC_{50} Evaluation of AGO and PMS on Fresh Water Crustacean *Desmoscaris Trispinosa* (72 Hours)

Toxicant	Conc. (mg/L)	Number surviving	Percentage (%) surviving	Percentage (%) mortality
AGO	0.05	19	100	0
	0.10	16	80	20
	1.00	13	65	35
	10.00	11	55	45
	100.00	5	25	75
PMS	0.05	20	100	0
	0.10	19	95	5
	1.00	18	90	10
	10.00	17	85	15
	100.00	15	75	25

TABLE 12
LC_{50} Evaluation of AGO and PMS on Fresh Water Crustacean *Desmoscaris Trispinosa* (96 Hours)

Toxicant	Conc. (mg/L)	Number surviving	Percentage (%) surviving	Percentage (%) mortality
AGO	0.05	18	90	10
	0.10	9	45	55
	1.00	7	35	65
	10.00	4	20	80
	100.00	0	0	100
PMS	0.05	19	95	5
	0.10	12	60	40
	1.00	9	45	55
	10.00	7	35	65
	100.00	4	20	80

Observed percentage mean mortality of the test shrimp in both the fresh and brackish water environments in relation to the control in a one-way ANOVA test were not significantly different at $p = 0.1016$, $F = 2.492$. The mean toxicity profile of the fresh and brackish water shrimp exposed to varying concentrations of petroleum hydrocarbons in the water habitats are presented in Table 1-12.

Lethal Concentration (LC_{50}) of the toxicant on the test organisms

Probit was used to determine the lethal concentration (LC_{50}) of the toxicants in the WSF in the test organisms. The acute toxicity evaluation of the toxicants gave the 96-hour LC_{50} values for freshwater and brackish water test habitats as 0.330mg/l and 1.986 mg/l, respectively, for AGO in comparison with the 96-hour LC_{50} values of 0.485mg/l and 2.919mg/l obtained for PMS in freshwater and brackish water test habitats, respectively.

Effect of concentration of water-soluble fractions on the percentage survival of test organisms

The effect of different concentrations of water-soluble fractions of PMS and AGO (0.05, 0.10, 1.00, 10.00, and 100.00 mg/l, respectively) on the test organism (*Paleamonetes africanus*) showed that there was a decrease in the percentage survival of the organism with an increase in the concentration of the toxicants and contact time. Although at lower concentrations (0.05 mg/l) for the water soluble fraction of both toxicants, there was no mortality after 48 hours, at higher concentrations of the toxicants (10.00 and 100.00 mg/l, respectively), the mortality was high, with the highest mortality recorded at 100.00 mg/l concentration of the toxicant, in which all organisms died after 96 hours for the AGO water soluble fraction and 60% mortality was recorded for the PMS water soluble fraction, as shown in Table 14. The higher concentration of the toxicant and the longer exposure period showed detrimental effects on the test organism. A 100 mg/l concentration at 96 hours was able to kill the entire test organism, bringing the mortality rate to 100 percent for the AGO toxicant. In any case, it was observed that there was a decline in the rate of survival with an increment in the concentration of the toxicant and an increment in the contact time for both toxicants, as outlined in tables 1–6.

However, in fresh water, on the other hand, there was a decrease in the percentage survival of *Desmoscaris Trispinosa* with an increment in the concentration of the toxicant and an expanding contact time (Exposure period). Concentrations of 0.05 and 0.1 mg/l did not record any mortality at the 24-hour exposure period; however, concentrations of 0.1 and 1.0 mg/l showed 20% and 35% mortalities recorded, respectively, for the AGO toxicant and 5% and 10% mortalities, respectively, for PMS at the 72-hour exposure period (table 19). The lowest concentration, 0.05 mg/l, after 72 hours of contact time had no inhibitory impact on the test organism (*Desmoscaris Trispinosa*) for both toxicants (table 19). It was observed that there were no survivors in the highest concentration of 100.00 mg/l after 96 hours of contact time with the AGO toxicant (table 20). Higher concentrations of 0.10, 1.00, 10.00, and 100.00 mg/l had the least negative effect on *Desmoscaris Trispinosa* as compared with the toxic effects of the toxicants on *Paleamonetes africanus* at the same concentrations in brackish water. A concentration of 0.05 mg/l was observed to demonstrate some rate of mortality on *Paleamonetes africanus* after 72 hours of exposure, while at a similar concentration and contact time, no mortality was recorded for *Desmoscaris Trispinosa*. In any case, at increasing concentrations of the toxicant and an expanding contact period, the rate of survival of the test organism (*Desmoscaris Trispinosa*) diminished, with no survivors at 100.00 mg/l concentration after a 96-hour exposure period for the AGO in fresh water, while PMS showed a mortality rate of 80% at the same concentration and exposure time. Concentrations of 0.05 mg/l showed little or no mortality rate after 48 hours of exposure to the two toxicants in fresh water.

The increasing concentration of the two contaminants (PMS and AGO) and the further expansion of contact time (exposure period) affected the test organism (*Desmoscaris Trispinosa*). It was observed that a diminishing rate of survival of the organism with increasing concentrations of toxicants and contact time was the pattern. The most elevated mortality of 100% was recorded in concentrations of 100.00 mg/l at a 96-hour contact period. The lower concentrations of 0.05, 0.10, and 1.00 mg/l had minimal negative impact, though higher concentrations of 1.00, 10.00, and 100.00 mg/l demonstrated the highest decrease in the rate of survival of the test organism with increasing time (tables 7–12).

Table 13: Physico-chemical properties of fresh water soluble fractions

PARAMTER	FRESH WATER	WSF (AGO) FRESH	WSF (PMS) FRESH
Temperature	25.00 ± 2	25.00 ± 2	25.00 ± 2
pH	6.8 ± 0.2	5.3± 0.2	5.8± 0.2
DO (mg/L)	6.8 ± 0.1	4.6± 0.1	4.4± 0.1
BODs (mg/L)	19.99 ± 0.02	47.99± 0.11	40.00± 0.02
COD (mg/L)	51.06 ± 0.20	131.06± 0.20	81.06± 0.20
Salinity (mg/L)	0.28	10.28	10.19
EC (µS/cm)	187±0.56	198±0.56	196±0.56
Turbidity (NTU)	15.65±0.10	20.85±0.10	19.95±0.10
TSS (mg/L)	9.90 ± 0.14	21.10± 0.14	19.20± 0.14
TDS (mg/L)	19.84 ± 0. 06	24.86± 0.06	24.84± 0.4
Phosphates,PO_4^{3-}(mg/L)	0.47±0.00	4.91±0.00	4.58±0.00
Nitrate NO_3^- (mg/L)	1.08±0.4	4.42±0.4	6.02±0.4
Sulphate SO_4^{2-} (mg/L)	0.82±0.01	3.47±0.01	3.47±0.01
Hydrogen carbonate. HCO_3^- (mg/L)	1.48±0.20	14.10±0.01	13.68±0.01
Calcium ion,Ca^{2+}(mg/L)	0.27±0.00	0.91±0.00	0.91±0.00
Magnesiumion,Mg^{2+}(mg/L)	0.82±0.00	1.21±0.00	1.60±0.00
NH_4-N (mg/ L)	0.16±0.01	0.16±0.01	3.31±0.01

Table 14: Physico-Chemical Properties of Brackish Water Soluble Fraction

PARAMTER	BRACKISH WATER	WSF (AGO) BRACKISH	WSF (PMS) BRACKISH
Temperature	25. 00± 2	25. 00± 2	25. 00± 2
pH	7.2 ± 0.2	5.50 ± 0.2	6.10 ± 0.2
DO (mg/L)	6.2 ± 0.1	5.00± 0.1	6.0± 0.1
BODs (mg/L)	17.53 ± 0.11	45.53± 0.11	39.98± 0.02
COD (mg/L)	59.18 ± 0.04	394.31± 0.04	346.24± 0.04
Salinity (mg/L)	13100	13110.28	13105
EC (µS/cm)	28600.5±0.5	28611±0.5	28609±0.5
Turbidity (NTU)	39.50±0.10	44.8±0.10	43.8±0.10
TSS (mg/L)	50.96± 0.14	60.98± 0.14	58.84± 0.14
TDS (mg/L)	506.55 ± 9.26	511.55± 3.26	511.55± 0.4
Phosphates, PO_4^{3-} (mg/L)	3.96±0.00	8.04±0.00	4.58±0.00
Nitrate NO_3^- (mg/L)	1.24±0.4	3.89±0.4	3.78±0.4
Sulphate SO_4^{2-} (mg/L)	2.59±0.01	5.24±0.01	3.74±0.01
Hydrogen carbonate HCO_3^-(mg/L)	2.10±0.20	14.30±0.20	13.68±0.20
Calcium ion, Ca^{2+} (mg/L)	0.38±0.00	1.02±0.00	0.91±0.00
Magnesium ion, Mg^{2+}(mg/L)	1.19±0.00	1.58±0.00	1.21±0.00
NH4-N (mg/ L)	0.29±0.01	0.29±0.01	3.44±0.01

The physico-chemical characteristics of the test solutions were determined at the beginning and end of the experiment. Some of the parameters tested include temperature, dissolved oxygen (DO), salinity, and hydrogen ion concentration (pH). Results obtained for physicochemical analysis of water samples showed a significant difference $p<0.05$ between the water soluble factions of AGO and PMS in brackish water and freshwater, respectively. The data in Table 13 and 14 shows that The mean pH were 5.50±0.02 and 6.10±0.02 for the water soluble fractions of AGO and PMS in brackish water respectively while the mean pH were 5.30±0.02 and 5.80±0.02 for the water soluble fractions of AGO and PMS in freshwater, respectively. The WSF of gasoline had the highest pH, while the pH of diesel was lower. The pH of the WSFs was significantly different from each other ($p < 0.05$).

Discussion

Median lethal toxicity concentration, LC_{50}

The acute toxicity evaluation of the toxicants gave the 96-hour LC_{50} values for freshwater and brackish water test habitats as 0.330mg/l and 1.986 mg/l, respectively, for AGO in comparison with the 96-hour LC_{50} values of 0.485mg/l and 2.919mg/l obtained for PMS in freshwater and brackish water test habitats, respectively.

The values obtained for the LC_{50} indicate that the freshwater shrimp *D. trispinosa* were more sensitive to the AGO and PMS than the brackish water shrimp *P. africanus*. It was observed that

the higher the LC_{50}, the lower the toxicity to the test organisms, and vice versa. The difference in response may be related to the relative activity levels of the species tolerance in the brackish environment, but the toxicants' mode of action values between the fresh and brackish water tests may not be the same. Similarly, the relative difference can be unconnected with the varying osmoregulatory demand observed in the mean percentage mortality and 96-hour LC_{50} of the different environments. It has been reported that in the freshwater environment, any physical damage to the external tissues of the organisms allows more water to enter the body and salt to escape, placing an additional burden on the kidneys and ultimately resulting in death. In the same vein, the buffering effect of the brackish water environment, as indicated by its higher pH range than the freshwater environment, could also have contributed to the observed lower effect on the brackish water shrimp. It has also been reported that the toxicity of chemicals can be altered by variations in water chemistry by affecting the amount of the chemical available to bind to organisms and sediment particles. At high concentrations, shrimp in both the freshwater and brackish water tests were observed to be immobilised. Although mortality is the most commonly used toxicity test endpoint, immobilisation is also ecologically relevant. There was however a progression of effect from low mortality to high mortality with increase in toxicant values or concentrations in both environments. This could be attributed to the increase in the concentration of the physicochemical parameters of the overlaying solutions on the water soluble fractrions as the concentration of the AGO and PMS increased. Both the freshwater and brackish water organisms were sensitive to the WSF of diesel and gasoline. This resulted in an increased percentage (%) death of the organisms with respect to time for the two toxicants.

Conclusion

The exposure of *D. trispinosa* to the water-soluble fractions of petrol (PMS) and diesel (AGO) fuel in fresh water and *P. africanus* in brackish water showed mortality even at low concentrations. The two petroleum hydrocarbons were found to have a lower LC_{50} in the test with fresh water shrimp when compared to that with brackish water shrimp. The data obtained from the Probit analysis for 96-hours median LC_{50} acute toxicity test indicate that the petroleum products were slightly toxic to bottom dwelling organisms in both the fresh and brackish water environments. Also, the insignificant difference between the LC_{50} and standard deviations of both aquatic environments indicates that the hydrocarbons would produce similar adverse effects irrespective of the environment they pollute, although with slight variations due to the differences in the physicochemical characteristics and environmental factors of both environments, which could predispose shrimp and other aquatic fauna to hydrocarbon toxicity. From the observed mortality and the LC_{50} for both petrol (PMS) and diesel (AGO), it follows that petrol (PMS) is less toxic to shrimps than diesel (AGO) in both habitat.

However, the freshwater test organisms were more sensitive to the petroleum products than the brackish water test organisms (Ezemonye et al, 2007). Wilde et al. (1983) observed that the toxicity of a chemical to aquatic organisms is dependent on the type of chemical, exposure duration, test organism, and environment. In the sequence of petroleum products toxicity, gill damage is the most obvious acute toxic effect; the immediate cause of death may be asphyxiation, but petroleum products may also be toxic internally. The interactions between petroleum products and proteins, and their influence on membrane permeability, could be the basis for the biological action of detergents (Abel, 2006).

Furthermore, due to the physiology of freshwater organisms, which have a greater body fluid concentration (about one-third), they are constantly taking in water by diffusion through their gills and skin for osmotic balance (Delbeek, 1983). Thus in a situation where there is damage to the skin and other tissues as is the case in exposure to high concentrations of petroleum products, there is an influx not only of water but also of the petroleum products leading to a higher toxicity of the chemical and death rate in the freshwater organisms (Bury et al, 1999). The difference in response between the fresh and brackish water shrimp may be related to the relative activity levels of the species tolerance in the brackish environment and the toxicant's mode of action (Bury et al, 1999). Petroleum products would dissolve and chemical compounds enters the environment and can cause severe harm or damage to aquatic organisms, especially bottom dwelling organisms (Adams et al, 1992).

With the findings from this study, appropriate safety measures such as adherence to standard operating procedures should be applied before the use and disposal of surfactant-containing chemicals since the test chemical was slightly toxic in both environments. This would ensure that the biotic components of the Nigerian Niger Delta ecosystem are prudently protected.

REFERENCES

Abel P.D. (2006) Toxicity of synthetic detergents to fish and aquatic invertebrates. Journal of Fish Biology. 6, (3), 279.

Adams W.J., Kimerle R.A., Barnett W.J. (1992) Sediment quality and aquatic life assessment. Environ. Sci. Technol. 26, (10), 1864

Adams WJ, Kimerle RA, Barnett WJ (1992). Sediment quality and aquatic life assessment. Environ. Sci. Technol. 26:1864-1874.

American Public Health Association (APHA) (2006). *Standard methods for the examination of water and wastewater*, 22nd Edition. American Public Health Association, America Water Works Association, Water Pollution Control Federation, Washington, DC. P. 1496.

American Society for Testing and Materials (ASTM) (1992). Standard guide for conducting 10-day static sediment toxicity tests with fresh and brackish and estuarine amphipods. In 1998 *Annual Book of ASTM Standards, Pesticides, Resource Recovery, Hazardous Substances and Oil Spill Responses, Waste Disposal, Biological Effects* 11:04.

American Society for Testing and Materials (ASTM) (1998), ASTM E 1367-92. Philadelphia, PA. pp. 732-757.

Anderson MB, Reddy P, Preslan JE, Fingerman M, Bollinger J, Jolibois L, Muheshwarudu G, and George WJ (1997). Metal accumulation in crayfish, *Procambarus clarkii* exposed topetroleum-contaminated Bayou in Louisiana. J. Ecotox. Environ. Saf. 37:267-272.

APHA (2012).Standard Methods for the Examination of Water and Wastewater, 20th Edn.American Public Health Association, Washington D.C. USA, 1213pp.

Aqua Sense (2004). The 10-day Marine Amphipod *Corophium volutator* Mortality Sediment Toxicity Test RIKZ/Specie-01. Report 2004.

ASTM (2010). Annual Book of ASTM Standards, part 24, Petroleum Products; Lubricants and Fossil Fuel, American Society for Testing and Materials 05–03: D4420–84.

ASTM (2012) Standard Guide for Conducting Static Acute Toxicity Tests with Echinoid Embryos.

ASTM E1563-98.ASTM International, West Conshohocken, Pennsylvania.

Atlas RM, Bartha R (1992). *Microbial Ecology: Fundamentals and Applications*, 3rd ed. The Benjamin/Cummings Publicating Company, Inc., Redwood City, C4065.

Bank PD, Brown KM (2002). Hydrocarbon effects on fouling assemblages; the importance of taxonomic differences and seasonal and tidal variations. Marine Environmental Research. 53:16:311-326.

Barron MG, Hansen J, Lipton J (2001). Association between contaminant tissue residues and adverse effects in aquatic organisms. Rev. Environ. Cont. Toxicol. 173:1-37.

Bat L, Gündogdu A, Sezgin M, Çulha M, Gönlügür G, Akbulut M (1999). Acute toxicity of zinc, copper, and lead to three species of marine organisms from the Sinop Peninsula Black Sea. Turk. J. Biol. 23:537-544.

Bohannon J, Bosch X, Withgott J (2002). Scientists brace for bad tidings after spill.Sci., 298: 296-297

Brassard PG (1996). Wetlands and Water Pollution. Boston College of Environmental Affair and Law Rev. 23(4): 885-919.

Bryant V, Newbery DM, McLusky DS, Campbell R (1985). Effect of temperature and salinity on the toxicity of nickel and zinc to two estuarine invertebrates (Corophium volutator, Macoma balthica). Mar. Eco. Prog. Ser. 24:139-153.

Bryant, P.J., Lafferty, C.M., and Lafferty, S.K. (1984). Reoccupation of Guerrero Negro, Baja California, Mexico, by grey whales. pp.375-87. In: M.L. Jones, S.L. Swartz, and S. Leatherwood (eds.) The Grey Whale, Eschrichtius robustus. Academic Press, Inc., Orlando, Florida. xxiv+600pp

Buikema A Jr., Neiderlehner BR, Cairns J Jr. (2000). The effects of a simulated refinery effluent and its components on the estuarine crustacean Mysidopsis bahia.

Burton AG Jr. (1992). Assessing contaminated aquatic sediments. Environ. Sci. Technol. 26:862- 1863.

Bury N..R., Mcgeer J.C., Wood C.M. (1999) Effects of altering freshwater chemistry on physiological responses of rainbow trout to silver exposure. Environ Toxicol Chem. 18, 49

Bury NR, McGeer JC, Wood CM (1999). Effects of altering freshwater chemistry on physiological responses of rainbow trout to silver exposure. Environ. Toxicol. Chem. 18:49-55
Chem. 64:81-108.

Ciarelli S, Vonck WA, Straalen NM (1997). Reproducibility of spikedsediment bioassays using the fresh and brackish benthic amphipod, Corophium volutator; fresh and brackish. Environ. Res. 43:329-343

Clemens, S.K.M., E. J., Neumanna, D. and Schroede J.I. (2009).Tolerance to toxic metals by a gene family of phytochelatin synthesis from plants and yeast.EMBO Journal18:3325-3333.

Dabestani, R. and Ivanov, I.N. (1999) A compilation of physical, spectroscopic and photophysical properties of polycyclic aromatic hydrocarbons. Photochemistry and Photobiology, 70, 10-34.

Dabestani, R. and Ivanov, I.N. (1999) A compilation of physical, spectroscopic and photophysical properties of polycyclic aromatic hydrocarbons. Photochemistry and Photobiology, 70, 10-34.

Dede E.B, Kaglo H.D. (2001) Aqua-toxicological effects of water soluble fractions (WSF) of Diesel fuel on O. niloticus fingerlings. J Appl Sci Environ Mgt; 5:93–6.

Delbeek C.J. (1987) Osmoregulation: Please give me a drink. Fish Biology. 1, 3,.

Delistraty D (1997). Toxic equivalency factor approach for risk assessment of polycyclic aromatic hydrocarbons. Toxicol. Environ.

DEPARTMENT OF PETROLEUM RESOURCES (DPR). (2002)Environment guidelines and standards for the petroleum industry in Nigeria (EGASPIN) Revised Edition, Universal Press, Lagos, Nigeria, pp. 276-297 ,

Dickson KL, Maki A, Brungs WA (1987). Fate and effects of sediment Bound Chemicals in Aquatic Systems. Pergamom Press, Elmsford, NY. pp. 219-244.

Ekundayo JA, Benka-Coker MO (1994). Effects of exposure of aquatic snails to sublethal concentrations of waste drilling fluid. Environ. Monitor. Asses. 30:291-297.

Environmental Protection Agency, EPA. U.S. Environmental Protection Agency (2000). Bioaccumulation testing and interpretation for the purpose of sediment quality assessment: status and needs. Bioaccumulation analysis workgroup, Washington, D.C. EPA/823/R00/00

Ezemonye L.I.N., Ogeleka D.F., Okieimen F.E. (2007) Biological alterations in fish fingerlings (*Tilapia guineensis*) exposed toindustrial detergent and corrosion inhibitor. Chemistry and Ecology 23, (5), 1

Jumoke, E., 1999. Comprehensive chemistry for senior secondary schools. A Johnson Publication Ltd Surulere, Lagos, Nigeria, pp 95-96

Khan ZM, Law FCP (2005). Adverse effects of pesticides and related chemicals on enzyme and hormone systems of fish, amphibians, and reptiles: A review. Proceed. Pakist. Acad. Sci. 42(4):315-323.

Lawson JW, Stenson GB, Mckinnon DG (1995). Diet of harp seals (Phoca groenlandica) in nearshore waters of the northwest Atlantic during 1990–1993. Can. J. Zool. 73:1805-1818.

Ma X, Ortalano L (2002). Environmental regulation in China, Rowman and Littlefield Publishers, Inc.

Marin, C.M.D.C. and Oron, G. (2007) Boron removal by the duckweed Lemna gibba: a potential method for the remediation of boron polluted waters. Water Research 41:4579–4584

National Research Council (2002). Oil spill dispersants on the sea. National Academic Press, Washington, D.C., P.126.

Nwachukwu A.N & Osuagwu, J.C. (2014). Effects of oil spillage on groundwater quality in Nigeria, American Journal of Engineering Research **3** (6):271 – 274.

Nwilo PC, Badejo OT (2005). Oil spill problems and management in the Niger Delta. Paper presented at International Oil Spill Conference, Miami, Florida, USA, May 2005. Oil and Gas Journal 2005.Oil and gas reserves in the Niger Delta of Nigeria.Oil and Gas Journal, 103 (41), November, 67–75.

Omofonmwan SI, Odia LO (2009).Oil exploitation and conflict in the Niger-Delta region of Nigeria. J Hum Ecol. 26:25–30.

Organisation for Economic Cooperation and Development (OECD) (2004). OECD Guidelines for the Testing of Chemicals No. 218: "Sediment-water chironomid toxicity test using spiked sediment" (adopted April 2004).

ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT OECD (2003). Environment, Health and Safety Publications Series on Pesticides Persistent, Bioaccumulative, and Toxic Pesticides in OECD Member Countries Results of Survey on Data Requirements and Risk Assessment Approaches No. 15, pp. 1-67

Peterson CH, Lubchenco J (2000). Marine ecosystem services. In: Nature's services societal dependence on natural ecosystems. Ed. By G. Daily. Island Press, Washington, D.C. P. 392.

Prince M, Sambasiram Y (1993). Bioremediations of petroleum wastes from the refining of lubricant oils. Environ. Prog. 12: 5-11

Propst TL, Lochmiller RI, Qualls CW Jr., McBee K (1999). In-situ (mesocosm) assessment of immunotoxicity risks to small mammals inhabiting petrochemical waste sites. Chem. 38:1049-1067.

Reish DJ, Oshida PS (1986). Manual of methods in aquatic environment research, Part 10, short-term static bioassays. FAO Fish Technical Paper 247: 62.

Samet JM, Dominici F, Curriero FC, Coursac I, Zeger SI (2000). Fine particulate air pollution and mortality in 20 U.S. cities. 1987-1994. New Engl. J. Med., 343:1742-1749.

Southerland E, Kravitz M, Wall T (1992). In Sediment Toxicity Assessment: Burton, G.A., Jr., Ed.: Lewis Publishers: Boca Raton, FL. pp. 341–370.

Sprague J.B. (1972). The ABC's of pollutant bioassay using fish. A paper presented on environment monitory in Los Angeles, California, June 27 – 28 (ASTM).

Stanislay P. (2000). Gas impacts on fish and marine organisms. Marine Pollution Bulletin, North America.

Temara, A.,Gulec, I., Holdway, D. (1999) Oil-induced disruption of foraging behaviour of the asteroid keystone predator, Coscinasterias muricata (Echinodermata). Marine Biology, 133, 501-507.

Tijjani, N, Ike, P.O., Usman, B.B., Malami, D.I& Matholo, A. (2012). Trace elemental analysis of Nigerian petroleum products using AAS method. InternationalJournal of Scientific and Engineering Research, **3** (2): 1– 5.

Towards Safe and Effective Use of Chemicals in Coastal Aquaculture. Reports and Studies, GESAMP. No. 65. Rome, FAO.

United States Environmental Protection Agency (1993). Provisional Guidance for Quantitative River Assessment of Polycyclic Aromatic Hydrocarbons EPA Office of Research and Development. EPA/600/R: 931089.

Ururahy AFP, Marins MDM, Vital RL, Therezinha, Pereira N Jr. (1998). Effect of aeration on biodegradation of petroleum waste. Revista de Microbiologia. 29(4):267-272.

Whale GF, Worden JR (1999). Direct Toxicity Assessment (DTA) of sediments collected in the vicinity of Forcados Oil Production Terminal. Shell Petroleum Development Company (SPDC) Exploration and Production, Report 47057, P. 10.

Wilde E.W., Soracco R.J., Mayack L.A., Shealy R.L., Broadwell T.L., Steffen R.F. (1983) Comparison of chlorine and chlorine dioxide toxicity to fathead minnows and bluegill. Water Res. 17, (10), 1327.

Willis KJ, Ling N (2003). The toxicity of Emamectin benzoate, an aquaculture pesticide, to planktonic marine copepods Aquac. 221:289-297.