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Full Length Research Paper

Effect of agricultural pesticides on the degradation of medium spill concentrations of Bonny light crude oil in a tropical rain forest soil

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The effect of three agricultural pesticides; K-othrin (deltamethrin), dichlorvos (2,2 dichlorovinydimethy phosphate) and carbofuran (2,3–dihydro–2,2-dimethylbenzofuran-7-y1methylcarbamate, on the degradation of medium spill concentrations of Bonny light crude oil in a tropical rain forest soil in the Niger Delta was investigated. Hydrocarbon (crude oil) loss within a 56-day period was monitored using photometric method. Mineralization (ultimate biodegradation) for the same period was monitored using the ratio of inorganic carbon to that of total organic carbon. Two positive control systems were employed one consisting of soil impacted with 5000 ml/m^2 of olive oil while the other consisting of soil impacted with 5000 ml/m^2 of crude oil. Negative control consisted of soil impacted with 5000 ml/m^2 of olive oil and 200 g of sodium azide. Other treatment options involved soils impacted with 5000 ml/m^2 of Bonny light crude oil with pesticide at manufacturers recommended doses and soil impacted with pesticides alone. Soil with no treatment also served as a test system. Results suggested that there was a significant difference at 0.05 probability levels in the percentage hydrocarbon left when the mean value of treatment with pesticide alone was compared with treatment with pesticide/crude oil mixtures. There was also a significant difference in the percentage hydrocarbon left when pesticide/crude oil mixtures treatments were compared with the two positive controls. Percentage hydrocarbon left decreased in the following order; Negative control > pesticide alone > pesticide/crude oil mixtures > crude oil alone > olive oil alone. Results suggested that percentage mineralization of organic carbon was greater in options involving pesticide alone when compared with options containing pesticide/crude oil mixtures. Percentage mineralization levels in pesticide/crude oil mixtures treatments were similar to values obtained in negative control and positive control involving crude oil. Percentage mineralization in treatments decreased in the following order; olive oil alone > pesticide alone > pesticide/crude oil mixtures = crude oil alone = negative control. Results showed that the application of pesticide to tropical soil impacted with medium spill levels of Bonny light crude reduced hydrocarbon degradation and mineralization in a 56 day period. Hydrocarbon degradation (loss) was significantly lower in pesticide alone options than in pesticide/crude oil mixtures suggesting possible enhancement of crude oil degradation in the latter treatments. Hydrocarbon loss was greater in crude oil alone options than in the other two treatments suggesting toxic influence of pesticide. Mineralization was, however, greater in pesticide alone options than in pesticide/crude oil mixtures suggesting greater degradability of these pesticides over pesticide/crude oil mixtures.

Key words: Pesticides, Bonny light crude oil, mineralization, hydrocarbon, treatment.

INTRODUCTION

In recent times the tropical rainforest soil of the Niger Delta has gained publicity as a result of deliberate (sabotage) and accidental pollution resulting from increased upstream (exploration and production) and downstream (refining) activities of the petroleum industry and the sensitive nature of the ecology (freshwater and brackish water mangrove, rainforest and marine environments) of this area (Okpokwasili and Odokuma, 1990). Crude oil spillage in terrestrial systems affects thousands of terrestrial species including bacteria (Okpokwasili and Odokuma, 1993; Odokuma and Okpokwasili, 1997). Some of the crude oil components are rapidly evaporated or biologically degraded (Atlas, 1981). Other components continue to remain several months and perhaps several years (Sentsova, 1979). Some of these components may be toxic to microorganism (Okpokwasili and Odokuma, 1993; Odokuma and Okpowasili, 1997) while some stimulate microbial activity especially at low concentrations (Gusev et al., 1981).

K-othrin, carbofuran and dichlorvos include the most commonly used pesticides in this area. Pesticides refer to an entire range of compounds, which include insecticides, herbicides, fungicides, rodenticides, bactericides, acaricides, nematicides, algicides and molluscicides (Sowunmi and Agboola, 1982). Pesticides are compounds containing both organic and inorganic moieties; they may be classified into different groups based on their chemical composition. These include organochlorines, organophosphates, carbamates, formamidines, thiocyanates, organotins, denitrophenols, synthetic pyrethroids and antibiotics (Bohmont, 1990). The pesticides are highly publicized class of environmental pollutants. Unlike other pollutants whose domain are restricted, pesticides spread to every part of the environment; soil, sediments, rivers, lakes, ponds, groundwater, ocean and even air. Certain pesticides have the ability to persist for a long time in the environment (Mirsra et al., 1996). Pesticides are subjected to chemical, biological or photochemical degradation in both soil and water (Howard, 1991). Direct and indirect discharges of industrial waste and accidental spillage also get enriched in the aquatic food chain through biodegradation, bioconcentration and biomagnification processes (Govindan et al., 1994).

Although pesticides are of great importance, their effect on non-target organisms is of great concern, as this poses a risk to the entire ecological system. Generally, the effects on microorganisms will vary depending on the chemical dosage, soil properties and various environmental factors (Ecobichon, 1991). Odokuma and Osuagwu (1994) have shown that the organochlorine, pesticides lindane and dieldrin were more toxic than organophosphate pesticides, pirimphos methyl and malathion to *Nitrsomonas, Nitrobacter* and *Thiobacillus.* The carbamates benomyl and methomyl were equally as toxic as the organochlorines to these microorganisms.

Pesticides can be transferred through volatilization, runoff, leaching, absorption and crop removal (Augustijn-Beckers et al., 1994). Biodegradation is increasingly being considered as a less expensive alternative to physical and chemical means of decomposing organic pollutants (Kuritz and Wolk, 1995). Odokuma and Ibor (2003) suggested that biostimulation could be used to accelerate bioremediation of crude oil. Okpokwasili and Nwosu (1990) in a related study reported that degradation of aldrin in the Nigerian environment by several bacterial genera is mediated predominantly by *Vibrio* and *Acinetobacter*. Odokuma and Omunakwe (2004) have shown that commonly used insecticides, Tetramethrin 0.3% (Mobil), Tetramethrin 0.2% (Red Raid), Pyrethrum (Blue Raid) and Propoxur (Baygon) are readily biodegradable in the rainforest soil of the Niger Delta.

K-othrin, carbofuran and dichlorvos include the most commonly used pesticides in the Niger Delta. K-othrin is a pyrethroid with the active component (S)-alpha-cyano-3-phenoxybenzyl *cis*-(1R 3R)-3-(2, 2-dibromovinyl)-2,2-dimethylcyclopropane carboxylate. It is employed as an insecticide. Dichlorvos (2, 2-dichlorovinyldimethyl phosphate) is an organophosphate and is employed as an insecticide. Carbofuran (2, 3-dihydro-2, 2-dimethylbenzofuran-7-yl methyl carbamate is employed as an insecticide, nematicide and a miticide. Both pesticides and crude oil contribute significantly to soil pollution. Pesticides are increasingly been employed to boost agricultural production in the Niger Delta especially to complement the ever increasing dependence by the residents of this area on the petroleum industry as an engine of economic growth.

The present study was, therefore, undertaken to determine the effect of commonly used agricultural pesticides (dichlorvos, k-othrin and carbofuran) on the degradability (hydrocarbon loss and mineralization) of medium spill concentrations of Bonny light crude oil in a typical rainforest soil of this area.

MATERIALS AND METHODS

Location and characteristics of experimental site

The experimental site was located beside the Multipurpose building of the University of Port Harcourt, located in Choba, Port Harcourt Rivers State, Nigeria. The study area was secondary grassland (originally rainforest), reasonably flat with slopes not exceeding 2^o. The area consisted of sand and clay deposit and the topsoil is loamy sand. The climate is tropical and the study period (August – October) coincided with rainy season. The soils were well drained.

Experimental design

The method employed was adopted from Odokuma and Ibor (2002). The site was 14 x 6 m in area. This was divided into nine test cells of 1 x 1 m, each using plywood of 45 cm which was buried 30 cm into the soil. The study area was duplicated about 10 m away in a similar environment. The period of testing was 56 days. Samples were collected and analyzed every two weeks (14 days).

Source of materials

Pesticides (dichlorvos, K-othrin and carbofuran) and olive oil employed were of analytical grade and were purchased from Bertram

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Chemical Limited Port Harcourt Nigeria. Bonny Light crude oil was obtained from Shell Petroleum Development Company (SPDC), Port Harcourt, Nigeria. Plywood was obtained from Timber market, Port Harcourt, Nigeria.

Sample application

The pesticides were applied to the relevant cells according to the manufacture's directives. K-othrin and dichlorvos (50 ml/m^2) were applied to relevant cells by the spray method. Carbofuran (25 g/m^2) was applied by broadcast method. Bonny Light crude oil (5000 ml) was sprinkled on relevant cells, to simulate a condition of a medium spill. Olive oil (5000 ml) was also sprinkled into one cell to serve as a positive control. Five thousand millilitres (5000 ml) of olive oil and 200 g of sodium azide were mixed and sprinkled into one cell to serve as negative control. Five thousand millilitres (5000 ml) of crude oil was also applied to one cell. They (pesticides, olive oil and crude oil) were worked into 15 cm depth of the soil.

Sampling schedule

Composite soil sampling (ten samples within a radius 500 cm apart were pooled together) was employed for soil sample collection. Samples were collected into well-labeled sterile polyethylene bag. About ten grams (10 g) of each test sample cell was collected for determination of physicochemical parameters while about 1 g was collected for microbiological analyses. Analyses were performed at two weekly intervals (Days 0, 14, 28, 42 and 56).

Microbiological analyses

The total bacterial count of soil samples was performed in triplicates on nutrient agar plates using the spread plate method (APHA, 1998). Plates were enumerated after 48 h of incubation at room temperature (28 ± 2C). The total pesticide-utilizing bacterial count of the soil samples was performed in duplicates on mineral salts medium of Mills et al., (1978) as modified by Okpokwasili and Odokuma (1990). The medium contained per litre 10.0 g NaCl; 0.42 g $MgSO_4.7H_2O$; 0.29 g KCl; 0.83 g KH_2PO_4; 1.25 g $NaPO_4$; 0.42 g $NaNO_3$; Agar 15 g. The pesticides (1% k-othrin, 1% dichlorvos and 0.1% carbofuran) were used as carbon and energy source. The mineral salt medium containing pesticide was also used in screening fungi for pesticide utilization. Potato dextrose agar was used to enumerate total fungal count of sample. Chloramphenicol was added to inhibit bacterial growth. Plates were enumerated after incubation at room temperature for 5 days.

Determination of physicochemical parameters

Soil physical properties such as porosity, bulk modulus, permeability, soil moisture and percentage sand, clay and silt were determined using procedures in British Standard Institute (1990). Total organic carbon was determined using Walkley – Black and Macro Kjeldahl methods, respectively (APHA, 1998). Soil pH was determined using PYE UNICAM PW 9418 pH meter fitted with a combined glass pH and reference electrode (APHA, 1998). Soil moisture content was determined by evaporation on Whatman filter paper No 1 (BDH Chemicals England) at 103°C in an electric oven. Phosphate was determined using Ascorbic acid method (APHA, 1998). Sulphate was determined using the turbidometric method (APHA, 1998). Ammonia was determined using the distillation method (APHA, 1998). Nitrate was estimated using the Brucein method (APHA, 1998) Total hydrocarbon levels were determined using the photometric method (APHA, 1998). Ten milligrams of the soil was mixed with 10 ml of carbon tetrachloride solution. This mixture was stirred and allowed to stand. The CCL_4 phase was decanted into a clean conical flask. Enough Na_2SO_4 (anhydrous) was added and shaken vigorously to remove all traces of water that may have been present in the mixture. The resultant clear solution was analysed spectrophotometrically at 420 nm using CCL_4 solution as blank. Hydrocarbon (oil and grease) concentrations in the water sample was extrapolated from a standard curve obtained by preparing various concentrations of the crude oil (0.10, 1.0 and 10.0 mg/ml) with absorbance's (0.01, 0.1 and 0.3) at 420 nm and calculated using the relationship.

Table 1. Description of treatment options.

Treatment	Description
KOA	K-othrin Alone (50 ml)
DCA	Dichlorvos Alone (50 ml)
CFA	Carbofuran Alone (25 g)
KO + CO	K-othrin (50 ml) and Crude oil (5000 ml)
CF + CO	Carbofuran (25 g) and crude oil (5000 ml)
O.oil	Olive oil (5000 ml)
O.O+ NaZ	Olive oil (5000 ml) and sodium azide (200 g)
C.oil	Crude oil (5000 ml)
NT	No Treatment

$$\%\ \text{Crude oil (ppm)} = \frac{\text{Conc. from graph X T.V.S.E}}{\text{Volume of sample (ml).}}$$

$$\text{Where T.V.S.E.} = \frac{\text{Total Volume of Solvent}}{\text{Extract (10ml)}}$$

Analyses of variance (ANOVA), Least significance difference (LSD) (Finney, 1978) were employed to determine the existence of significant statistical variations in the results.

RESULTS

In Table 2 pesticide characteristics are presented. K-othrin is an emulsion in water concentrate pyrethroid insecticide. Dichlorvos is an organophosphate insecticide aerosol while carbofuran is a liquid carbamate insecticide. Physical parameters of the soil before treatment (Table 3) revealed that the soil was predominantly sandy with a loamy sandy soil texture. The hydrocarbon level (Table 4) revealed a decrease with time in most treatment options. Options KOA, DCA and CFA showed a slight insignificant increase at 95% confidence limits compared to before treatment levels (NT). Options KO+CO, DC+CO and CF+CO recorded very high hydrocarbon levels after treatment.

The percentage hydrocarbon levels (Table 5) showed a decrease with time for all treatment options except for the negative control and the no treatment option. There was a significant difference in the percentage hydrocarbon left when the mean of treatment with pesticides alone (KDC not indicated in Table 2) was compared with the mean of treatment with pesticide / crude oil mixtures (OCF not indicated in Table 1). The F_{cal} = 9.53 while F_{Tab} was 3.88

Table 2. Pesticide characteristics.

Common name	Trade name	Formulation	Class of organic compound	Active component	Target organism
K- othrin	Aqua-K othrine	Emulsion in water concentrate	Pyrethroid	(S) – alpha – cyano -3 phenoenybenzyl cis-(IR. 3R) – 3 – (2,2, dibromovinyl) – 2,2-dimethyl cyclopropane carboxylate (Deltamethrin)	Insecticide
Dichlorvos	Didivane (DDVP)	Aerosol and soluble concentrate	Organopho sphate	2,2-dichloro vinyl dimethyl phosphate	Insecticide
Carbofuran	Carbosip Furadan	Liquid and granular formation	Carbamate	2,3-dihy dro-2,2-dimethyl benzofuran -7-yl methyl carbamate	Insecticide Nematicide mites

Table 3. Physical parameters of the soil before treatment.

Parameter	Value
Alkalinity	80±5.0 mg/kg
Bulk density	1.48± gkm^3
Moisture	75 ±1.5%
Permeability	2.14x10^{-3} cm/sec
pH	6.5±0.3
Porosity	42.70 ±4.5%
Clay	9.40±2.0 %
Sand	83.40±8.0 %
Silt	9.72 ±1.4%
Soil texture	Loamy sand

at 95% confidence levels when the two options were compared indicating that the % hydrocarbon left was significantly lower in the mean of treatment with pesticide and crude oil than the mean of treatment with pesticide alone. KDC is derived from the mean of options KOA, DCA and CFA while OCF is derived from the mean of options KO+CO, DC+CO and CF+CO

There was no significant difference in the % hydrocarbon left when KDC was compared with O.oil (positive control 1), F_{cal} = 4.4 while F_{tab} = 3.88, indicating that % hydrocarbon left was lower in O. oil than KDC. There was a significant difference in the % hydrocarbon left when OCF was compared with O.oil. F_{cal} = 4.81 while F_{tab} was 3.88 indicating that the % hydrocarbon left in O.oil was significantly smaller than that of KDC. There was a significant difference in the % hydrocarbon left when KDC was compared with C. oil (positive control 2), F_{cal} = 4.42 while F_{tab} = 3.88, indicating that the percentage hydrocarbon left in C. Oil was significantly lower than that of KDC. When OCF was compared with C. oil, F_{cal} was 4.08 while F_{tab} was 3.88, indicating that the % hydrocarbon left in C. Oil was significantly lower than that of OCF.

These results suggest that hydrocarbon loss was least in options containing pesticide alone and negative control. This was followed by options containing pesticide crude oil mixtures. Percentage hydrocarbon loss was greatest in positive controls (O. oil followed by C. oil option). The trend was as follows: negative control < pesticides alone < pesticide/crude oil mixt. < C. oil < O. oil.

There was a significant difference in the % mineralization when KDC was compared with OCF, F_{cal} = 4.97 while F_{tab} = 3.88 indicating that the % mineralization in KDC was significantly greater than that of OCF (Table 6). When KDC was compared with negative control the F_{cal} = 6.86 while the F_{tab} = 3.88 indicating that the % mineralization in KDC was greater than that of the negative control. When KDC was compared with one positive control 1, F_{cal} = 11.7 while F_{Tab} = 3.88 indicating that % mineralization in positive control 1 was significantly greater than that of KDC. When KDC was compared with the positive control 2 (C.oil), F_{cal} = 4.32 while F_{Tab} = 3.88, indicating that % mineralization in KDC was higher than in C.oil. There was no significant difference in the % mineralization between OCF and negative control. The F_{cal} = 0.39 while the F_{tab} = 3.88. A similar observation was made when OCF was compared with C.oil, the F_{cal} = 0.96 while the F_{tab} = 3.88. When C. oil was compared with negative control (0.0+NaZ) the % mineralization were similar i.e. F_{cal} = 1.92 while F_{Tab} = 3.88. The percentage mineralization was greater in 0. oil when it was compared with OCF. F_{cal} = 13.22 while F_{Tab} was 3.88. A similar observation was made when O. oil was compared with negative control; F_{Cal} = 15.98 while F_{tab} = 3.88. When the two positive controls were compared with each other, F_{cal} = 11.77 while F_{Tab} = 3.88 indicating that the % mineralization in O. oil was significantly greater than C. oil.

These results indicate that mineralization was greatest in positive control 1 (O.oil) and least in the negative control (O.O + NaZ). Percentage mineralization was greater in option involving pesticides alone when compared with option containing pesticide/crude oil mixtures. The percentage mineralization in pesticide/crude oil mixtures (OFC) was similar to that of negative control and

Table 4. Hydrocarbon concentrations of test systems (mg/Kg).

Treatment	Days				
	0	14	28	42	56
KOA	7.05	5.04	4.60	4.36	4.28
DCA	7.55	5.1	4.70	4.38	4.30
CFA	7.86	5.12	4.76	4.40	4.34
KO+CO	10017.00	8610.00	7400	6000.12	4800.22
DC+CO	1017020	8660.10	7450.22	6860.00	5220.06
CF+CO	10170.30	8700.20	7800.62	7000.14	5600.12
O.O+NG	3000.40	2200.00	1800.12	1100.44	860.22
O.oil	2980.00	1900.94	1000.88	600.61	400.00
C.oil	10100.00	8080.10	6000.2	4100.00	2061
NT	4.10	4.12	4.13	4.11	4.12

Table 5. Percentage hydrocarbon left in treatment options.

Treatment	Days				
	0	14	28	42	56
KOA	100	71.48	65.2	61.8	60.7
DCA	100	67.5	62.3	58.0	56.9
CFA	100	65.13	60.5	55.9	55.2
KO+CO	100	84.6	72.7	58.9	47.2
DC+CO	100	85.2	72.7	67.4	51.3
CF+CO	100	85.5	76.6	68.8	55.1
O.O+NaZ	100	98.0	97.6	96.6	96.2
O.oil	100	63.7	33.5	20.13	13.4
C.oil	100	80.0	59.4	40.5	20.3
NT	100	100	100	100	100

Table 6. Percentage mineralization of treatment options.

Treatment	Days				
	0	14	28	42	56
KOA	75.23	46.99	49.38	55.41	63.77
DCA	56.80	42.68	41.73	50.00	61.90
CFA	54.76	41.61	40.29	44.44	53.28
KO+CO	46.40	24.40	23.08	33.82	41.00
DC+CO	46.36	22.57	21.05	28.13	35.17
CF+CO	45.80	21.20	18.28	25.67	30.50
O.O+NaZ	41.12	19.23	17.86	16.98	16.08
O.oil	60.00	64.44	72.99	81.57	85.14
C.oil	50.98	32.10	31.00	40.35	47.18
NT	70.00	71.88	73.44	47.60	75.40

positive control 2 (involving crude oil alone). There was no significant difference between the percentage mineralization of the positive control 2 and the negative control. The trend was as follows, % mineralization was greatest in O.oil > pesticide alone > pesticide/crude oil mixt. = crude oil alone = negative control.

The total heterotrophic bacterial and fungal counts for the various treatment options (Figures 1 and 2) revealed an increase with time for most options. The negative control showed a slight decrease in counts from day 0 to

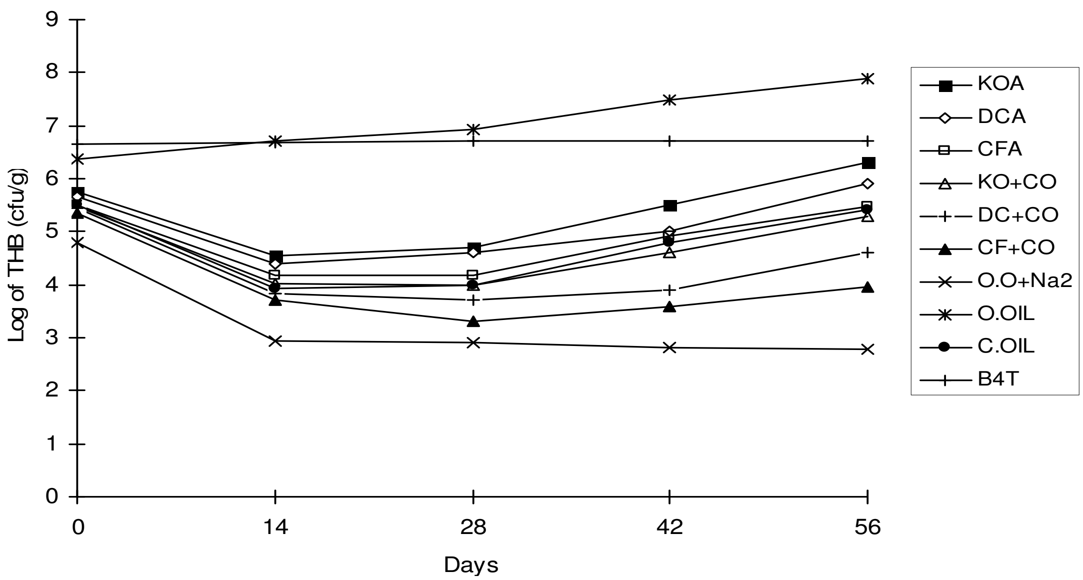

Figure 1. Growth of total heterotrophic bacteria (THB).

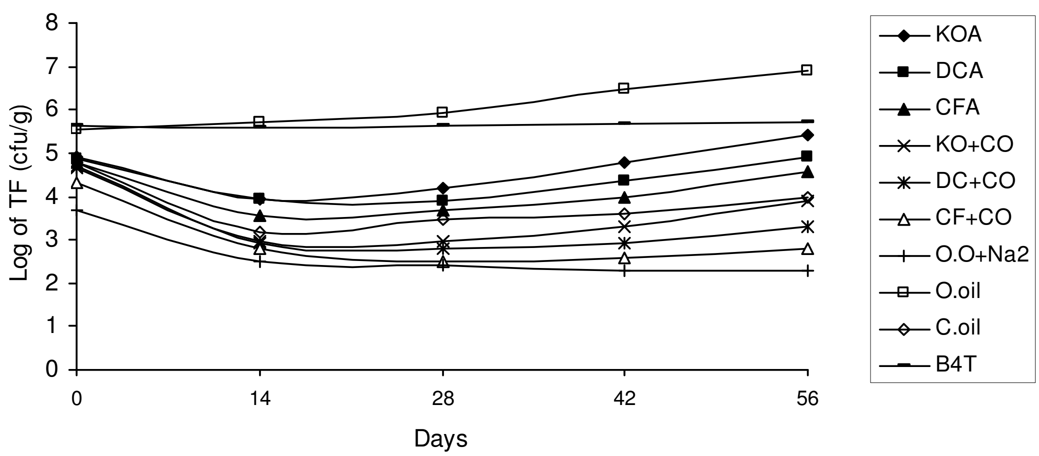

Figure 2. Growth profile of total fungi (TF).

day 14 which stabilized between day 14 and 56. The increase in count for the no treatment option (NT) with time was insignificant. The pesticide utilizing bacteria (PUB) and pesticide utilizing fungi (PUF) in Figures 3 and 4 showed an increase with time.

The pH and alkalinity of most of the options (except both positive controls and the no treatment option) decreased with time (Figures 5 and 6). The pH of the positive controls increased with time while the pH of the no treatment option remained relatively constant with time.

The ammonium ion level (Figure 7) decreased with time for all options except the no treatment option. The nitrate levels decreased till day 14 and 28 for most options then began to increase by day 42 and 56 (Figure 8). There was no change in the nitrate level for the no treatment option. Sulphate results revealed a similar trend (Figure 10). The phosphate levels for the negative control and the no treatment option (Figure 9) were constant throughout the experiment. Other treatment option revealed a decrease with time.

The total organic carbon (TOC) and inorganic carbon (IC) levels (Figures 11 and 12) decreased with time for most option except for the no treatment option and the negative control which remained constant in TOC throughout the period. The increase in the IC was only from day 0 to day 14 for most option. After day 14 there began a decrease to day 28 which was then followed by an increase in day 56, just like in TOC the IC of the no treatment option remained constant throughout the pe-

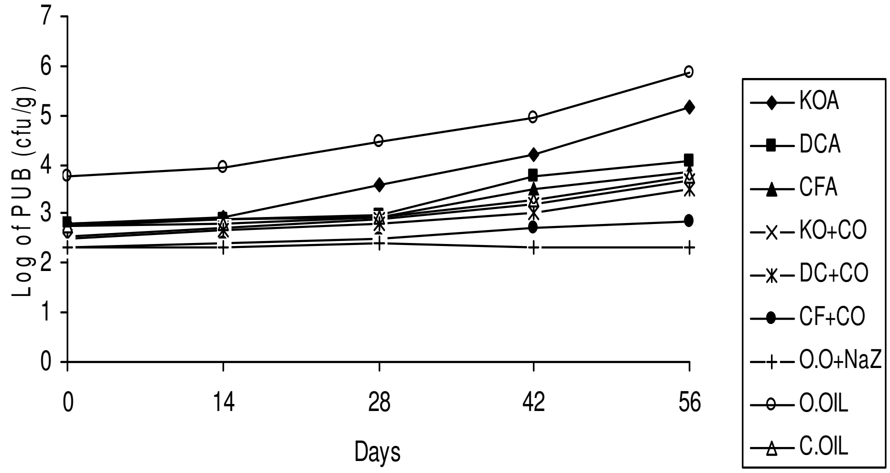

Figure 3. Growth profile of pesticide utilizing bacteria (PUB).

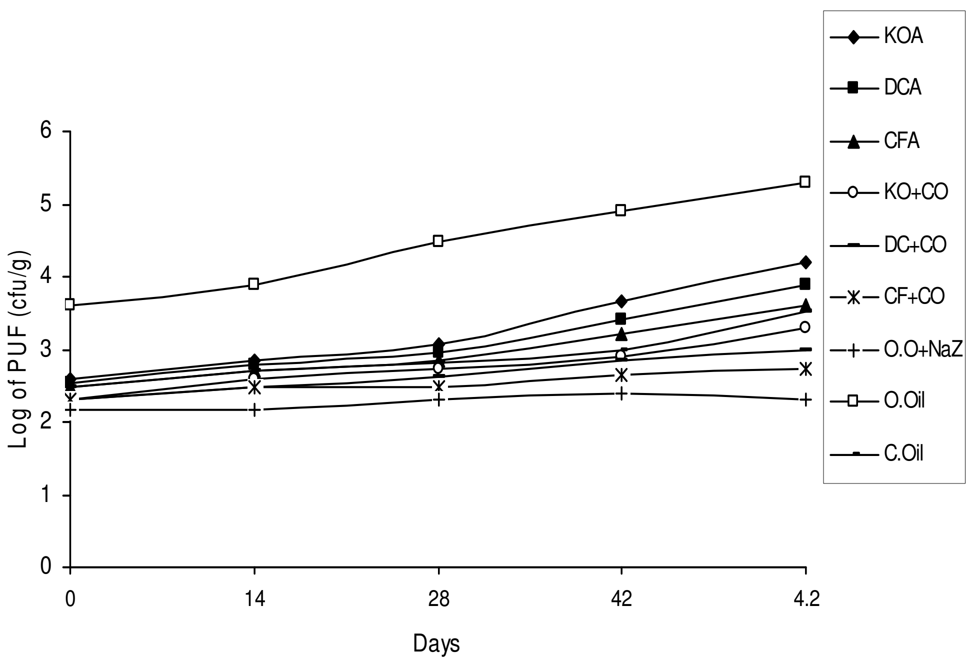

Figure 4. Growth of profile of pesticide utilizing fungi (PUF).

riod. However, the IC of the negative control decreased throughout while the IC of O. oil (positive control 1) increased throughout the period.

DISCUSSION

The reduction in hydrocarbon levels with time in this study is attributable to physical, chemical and biological agents of weathering (Odokuma and Ibor, 2002; Odokuma and Dickson, 2003). The percentage hydrocarbon left after a 56 day period showed the following trend: Negative control = no treatment option pesticide alone > pesticide/crude oil mixture > C. oil > O. oil.

The results obtained for the negative control is attributable to the reduction in the population of hydrocarbon utilizing microorganism (Figures 1 and 2). Sodium azide is very toxic to heterotrophic bacteria and fungi (Odokuma and Okara, 2005). In the no treatment option hydrocarbon levels had reached natural levels thus the constancy in the low levels of hydrocarbon with time.

Hydrocarbon levels in options containing pesticide

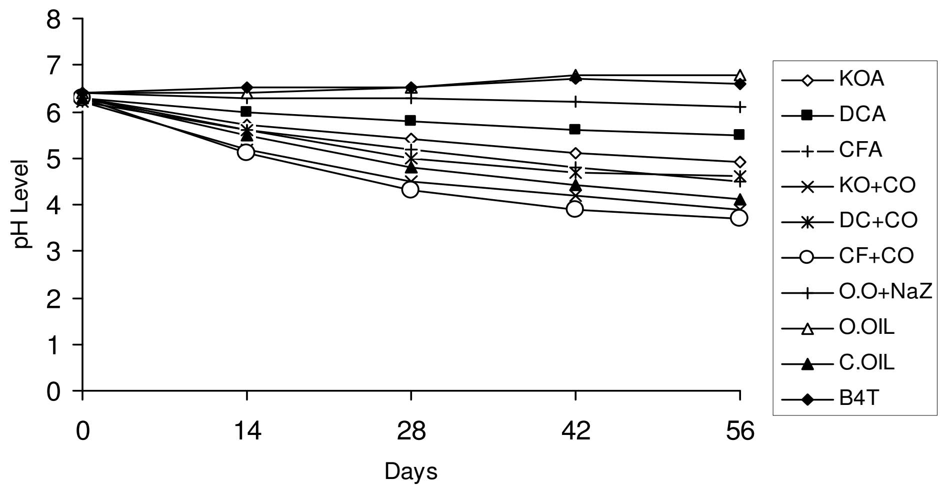

Figure 5. pH level of soil sample.

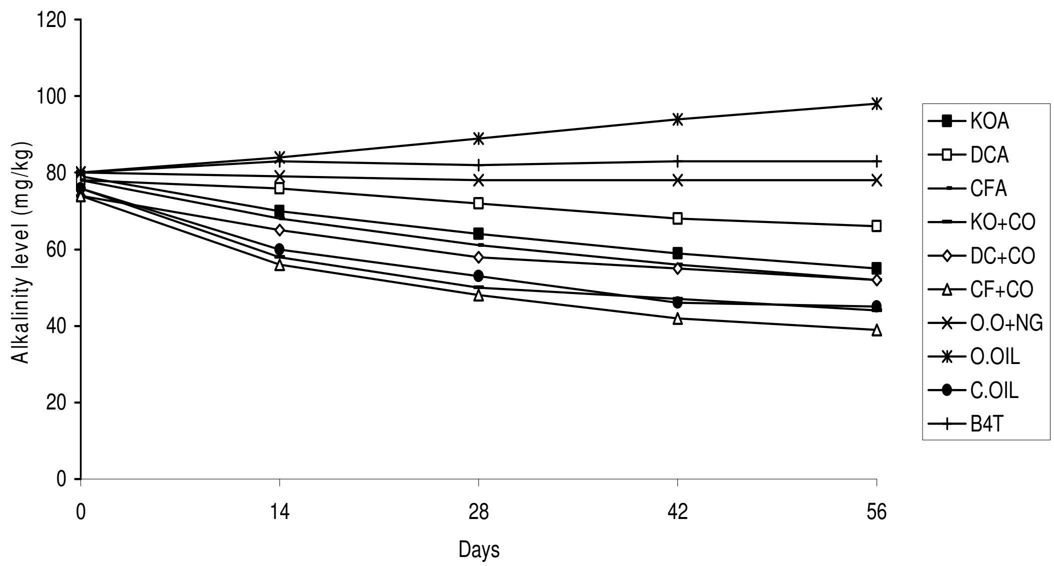

Figure 6. Akalinity level of soil sample mg/kg.

alone compared with those options containing pesticide /crude oil mixtures indicated that degradation of crude oil hydrocarbons was greater in the pesticide/crude oil mixtures. More crude oil in options containing pesticide /crude oil mixtures may have stimulated hydrocarbon degradation. The concentration of crude oil in pesticide alone treatment had already reached biogenic levels so hydrocarbon degradation may have reached equilibrium with the environment. Addition of a degradable substrate crude oil now shifted the equilibrium thereby promoting further degradation of hydrocarbon.

The hydrocarbon levels left when pesticide/crude oil mixtures options were compared with crude oil alone option was significantly higher for the former. This suggested that the application of pesticide significantly affected the hydrocarbon degradation process. Combined toxicity of both pesticide and crude oil may have been responsible for this observation Okpokwasili and Odokuma (1993) have shown that 6 Nigerian crude oils inhibited nitrite utilization, nitritase enzyme activity and cellular integrity of *Nitrobacter*. Odokuma and Osuagwu (2004) observed that chemolithotrophic bacteria (*Nitrobacter, Nitrosomonas* and *Thiobacillus* were sensitive to commonly used carbamate (Benomyl and Methomyl) and organochlorine (Lindane and Dieldrin) pesticides.

The % hydrocarbon left in pesticide alone options when compared with the two positive controls (O. oil and C. oil) may be attributable to toxicity of pesticides. Similar observations may be adduced when comparing options containing pesticide/ crude oil mixtures with olive oil and

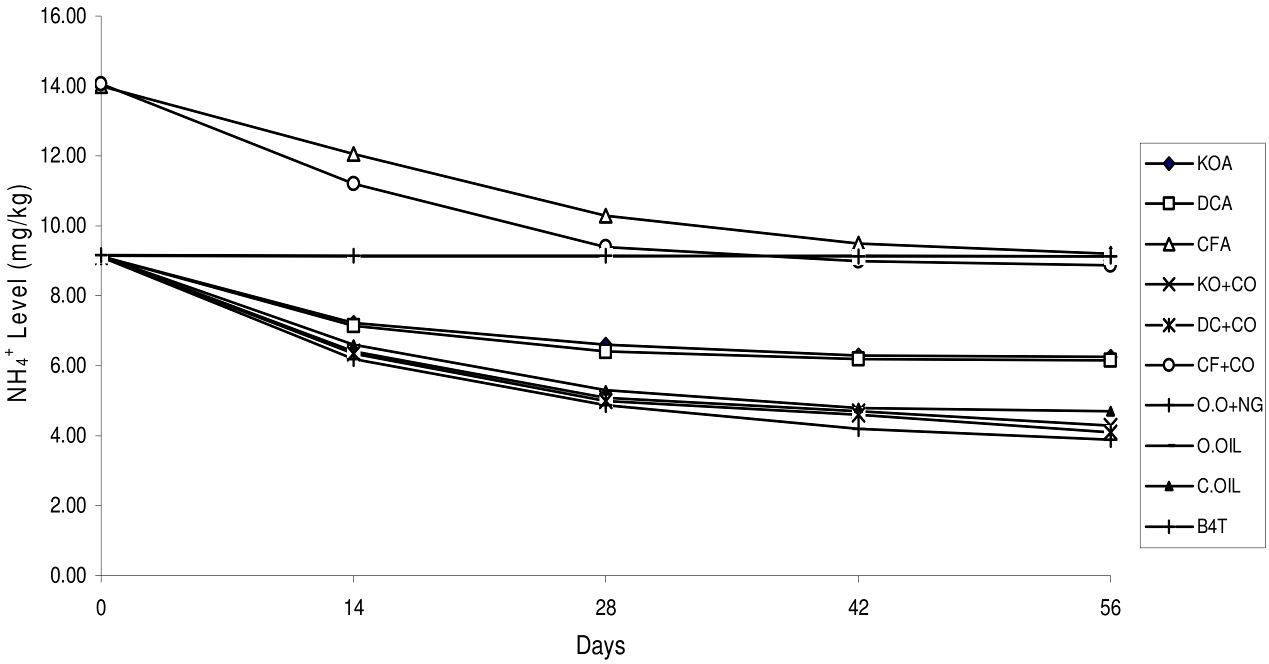

Figure 7. NH_4^+ level of soil sample (mg/kg).

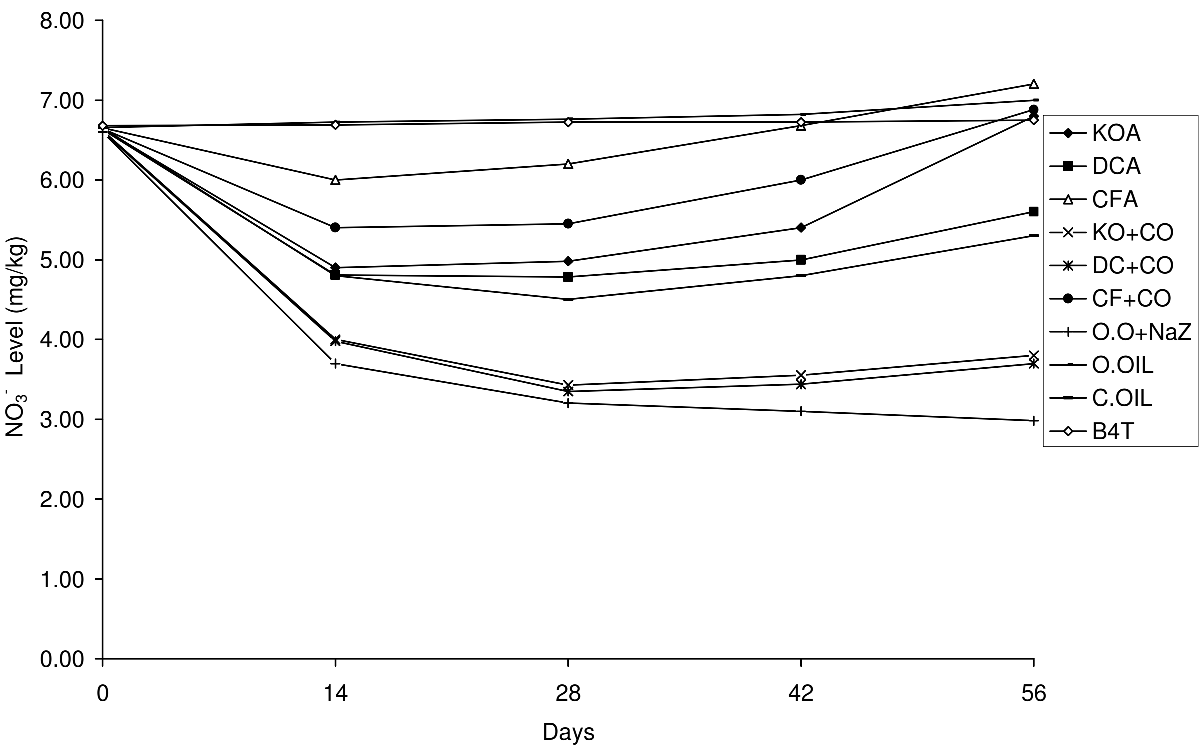

Figure 8. NO_3^- level of soil sample (mg/kg).

crude oil positive controls. Combined toxicity of pesticides /crude oil mixtures may have reduced hydrocarbon degradation in these options.

However, percentage mineralization was greater in options containing pesticide/crude oil mixtures. This was the converse of the hydrocarbon loss results. Mineraliza-

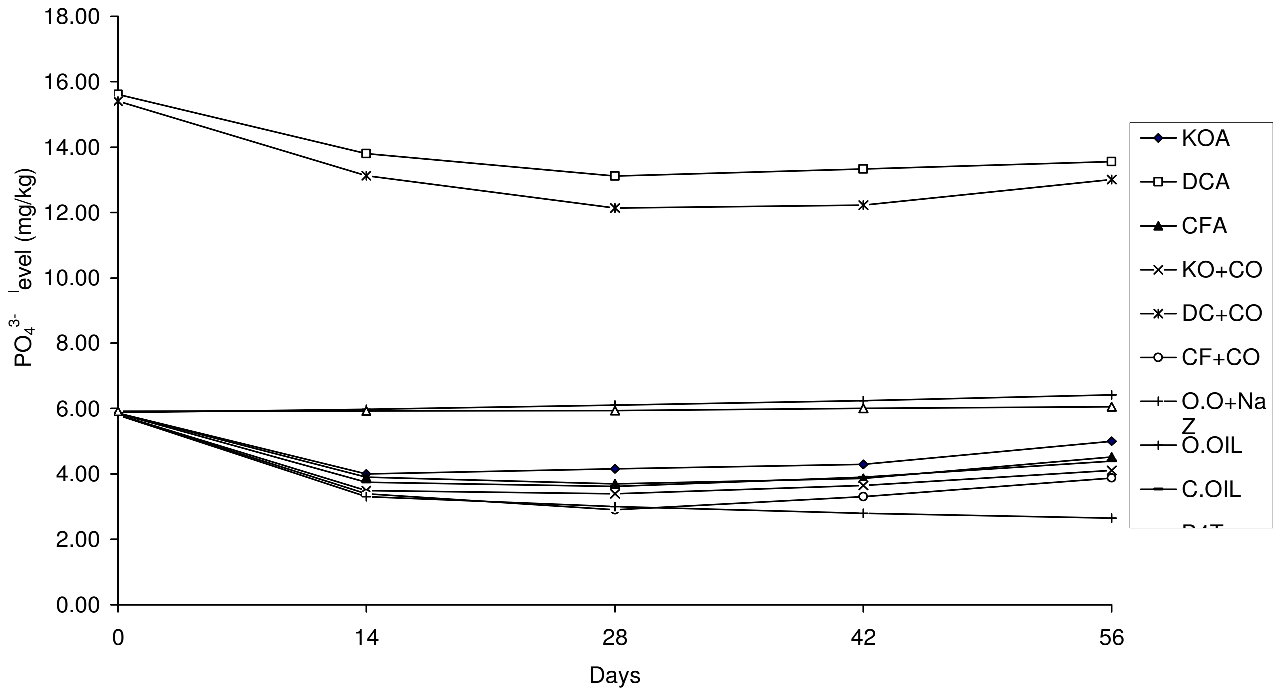

Figure 9. PO_4^{3-} level in soil sample (mg/kg).

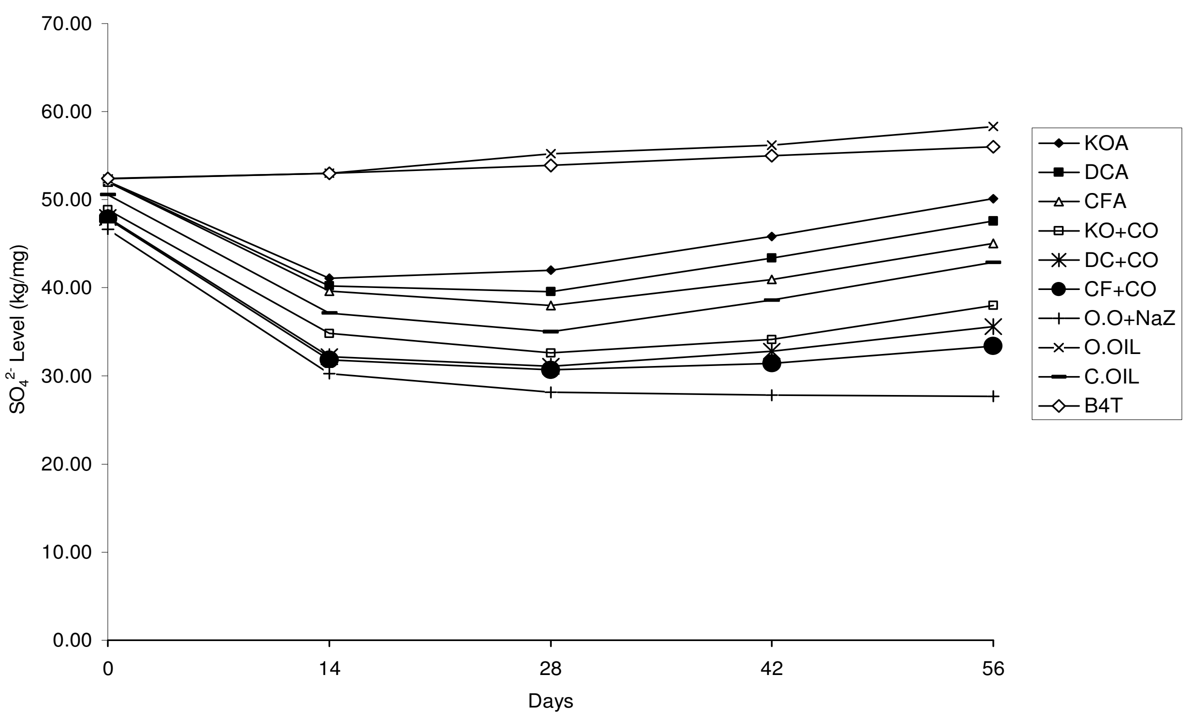

Figure 10. SO_4^{2-} level in soil sample (mg/kg).

tion involves the complete conversion of organic carbon into carbon dioxide water and energy in the presence of oxygen (Stiff, 1978). Hydrocarbon loss or degradation does not necessarily mean mineralization. It may mean hydrocarbon transformation to less detectable intermediates by the analytical method employed. Thus pesticide

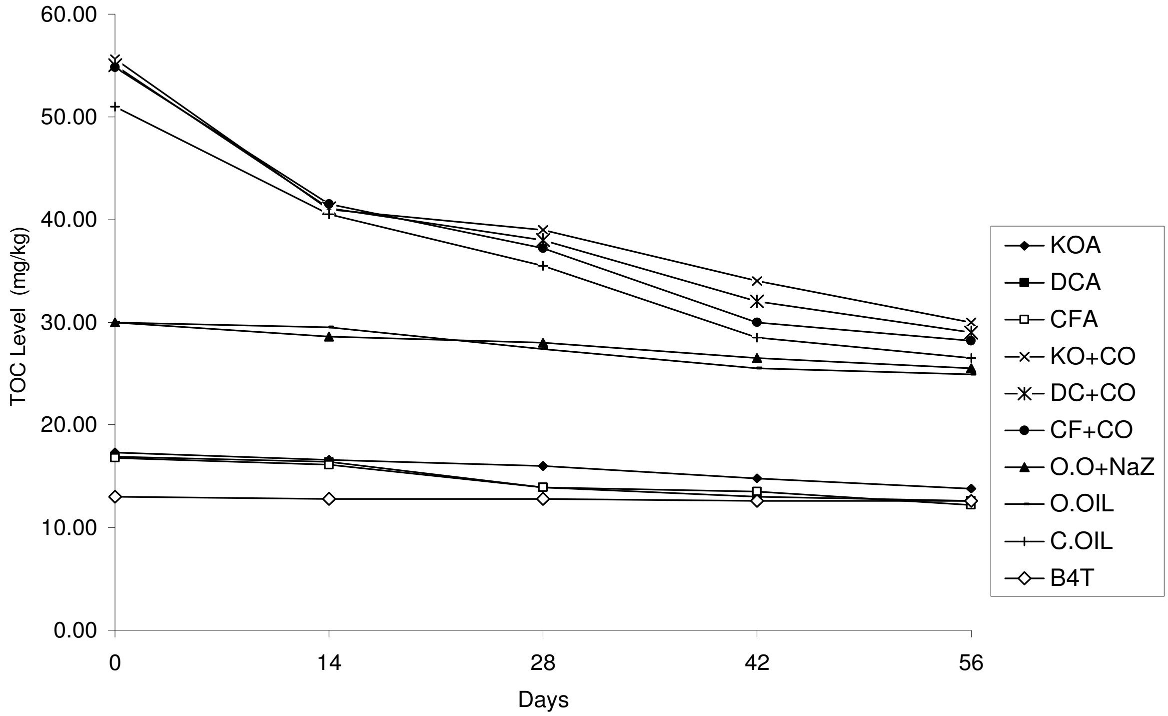

Figure 11. Total organic carbon level in soil sample (mg/kg).

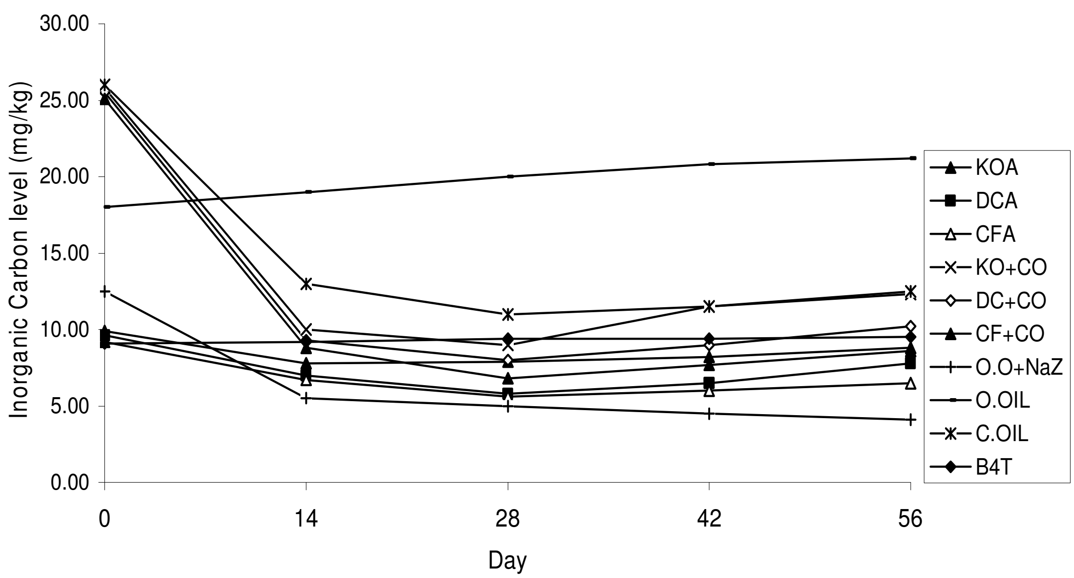

Figure 12. Inorganic carbon level in soil sample (mg/kg).

/crude oil mixtures option though revealing higher levels of hydrocarbon degradation still contained higher organic un-mineralized organic matter (pesticide and intermediates of crude oil degradation) when compared with options containing pesticide alone thus, their lower levels of mineralization. Odokuma and Omunakwe (2004) have shown that commonly used insecticides tetramethrin 0.3% (Mobil) tetramethrin 0.2% (Red raid), pyrethrum (Blue Raid) and propoxur (Baygon) are readily biodegradable in rain forest soil of the Niger Delta.

The level of percentage mineralization of pesticide /crude oil mixtures options were similar to those of negative control and positive control 2 indicating that the constituents of these options inhibited mineralization. Odokuma and Okpokwasili (1992) have shown that composition of oil spill dispersants affected their degradability.

Odokuma and Ikpe (2003) have reported that the composition of drilling muds affected their degradability and toxicity to *Nitrobacter Palaemonetes* and *Melampus.* Water based muds were more biodegradable than oil based mud while oil based mud were more toxic to these organisms than water based mud.

The increase in microbial counts (total heterotrophic bacteria, total fungi, PUB and PUF) with time in most of the treatment options is an indication of utilization of the organic compounds in these options. Observations by Odokuma and Omunakwe (2004) support these results. Odokuma and Dickson (2003) have shown that Bonny light is biodegradable in the Niger Delta dry lands and wetlands. The increase in microbial counts was greater in pesticide alone treatments than in pesticide/crude oil mixtures. Combined toxicity of both pesticide and crude oil may have been responsible for this observation.

The decline in pH and alkalinity for most of the treatment options (except in the two positive controls and the no treatment option) with time may be due to the production of acidic metabolites (Delyan et al*.,* 1990). Odokuma and Akpokodje (2004) have attributed the steady decline in pH in a simulated landfill leachate in a tropical soil to microaerophilic and anaerobic degradation of oil into fatty acids and alcohol. Odokuma and Okara (2004) attributed the pH of various treatments to be a function of the chemical composition of the treatment, which was related to the nature of the carbon source and other nutrients present. The decrease in the concentrations of ammonium nitrate and phosphate with time for most treatment options (except the negative control) and the no treatment option which remained constant indicated their utilization by microorganism during the degradation process. Similar observations have been made by Odokuma and Akpokodje (2004) and Odokuma and Okara (2004).

Conclusion

The application of pesticides to tropical soil impacted with medium spill levels of Bonny light crude recorded higher hydrocarbon losses in treatments involving pesticide /crude oil mixtures when compared with pesticide alone options suggesting possible enhancement of crude oil degradation. Hydrocarbon loss was greater in the second positive control (C.oil) than in both these options suggesting toxic effect of pesticides. Percentage mineralization in treatment options were however, greater in pesticide alone options than in pesticide/crude oil mixtures suggesting combined toxic effect of both constituents on resident soil microflora and the degradability of these pesticides.

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