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REMEDIATION OF MILD CRUDE OIL POLLUTED FRESH WATER WET LAND WITH ORGANIC AND INORGANIC FERTILIZER

Ibe Francis Chizoruo[1a*] Ibe bridget Onyekachi[2b], Ikpa Chinyere Benardette Chinaka[1c] and Eneldoh Magaret Chinyelue[1d]

[1]Department of Chemistry, Imo state University, P M B 2000 Owerri, Imo State, Nigeria.

[2]Department of Physical and Health Education, Alvan Ikoku Federal College of Education Owerri, Imo State Nigeria.

[*a]francispavo@imsu.edu.ng, [b]mavisbright@yahoo.com, [c]ikpacbc@gmail.com and [d]megnedoh @yahoo.com

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ABSTRACT. Wetland pollution due to inputs from crude oil is one of the most prevalent environmental problems facing the aquatic ecosystem in the world. The present study was intended to investigate the effectiveness of combination of cow lumen and NPK fertilizer in stimulating the degradation of crude oil polluted fresh water wet land. Soil samples were collected from unpolluted plots, crude oil polluted plots and crude oil polluted plots that were treated with the remediating agents. After fifteen days and sixty days of remediation, the soil samples were analysed for pH, electrical conductivity (E.C), phosphate, PO^{3-}_4, phosphorous, P, % organic carbon, % total nitrogen N, carbon/nitrogen ratio and total petroleum hydrocarbon, TPH. The result indicates that combination of the inorganic and organic manure was more efficient in stimulating the degradation of the crude oil than the use of either the cow lumen or NPK fertilizer alone. The physiochemical properties of the soil in all the treated plots were observed to have been improved when compared with that of the untreated plots.

INTRODUCTION

The increased demand for petroleum as a source of energy is a major anthropogenic source of crude oil pollution of the environment across the globe [1]. Crude oil pollution effects found in soil, water and air environments have continued to be a major issue of scientific concern, political and public interest [1]. The invention of internal combustion engines and its usage in all forms of transportation enlarged the demand for petroleum; this in turn increased the production, transportation, stockpiling, and distribution of crude oil as well as the by-products [2]. These activities and others pose serious environmental pollution risk which could be reduced, but not easy to be totally eliminated [3]. Soils which are contaminated by hydrocarbons have extensive damage of local ecosystems since accumulation of pollutants in animals and plants tissues may cause death or mutation [4].

The impact of crude oil pollution on the environment is enormous. Crude oil and its derivatives affect the soil by reducing its nutrient content [5.6]. It increases the toxic effect of heavy metals on the soil [7], and as a result of its hydrophobic characteristics crude oil reduces water infiltration into the soil [8]. Crude oil introduces non-organic, carcinogenic and growth-inhibiting chemicals present in the crude oil together with their toxicity to microorganism and man [9].

Coastal wetlands can be classified into tidal salt marshes, tidal fresh water marshes, and mangrove swamps [10]. Tidal freshwater marshes are wetlands found inland from the salt marshes but still close enough to the coast to experience fresh water tidal effects. Since these wetlands lack the salinity stress of salt marshes, they are often very productive ecosystems and dominated by a variety of grasses, perennial and annual broad-leafed aquatic plant [11]. Wetlands provide natural barriers to shoreline erosion, habitats for a wide range of wildlife including endangered species, and key sources of organic materials and nutrients for marine communities [10,12]. The impact of crude oil pollution on wetland ecosystems have been described and reviewed extensively [13,14,15,16,17].

The ecosystem of freshwater wetland has very low level of dissolved oxygen. Crude oil degradation is more feasible under aerobic condition, therefore the low level of oxygen in wetlands has the detrimental effects and makes clean up or remediation of the wetlands complex [18]. The addition of nutrients to crude oil polluted wetland has been shown to increase the degradation of oil [19,20,21,22].

The need for this research has become necessary owning to the fact that Imo State is a part of Niger Delta area of Nigeria and up to one third of the Niger Delta area is made of wetlands [23]. The Niger Delta area is made of rivers, creeks, estuaries and stagnant swamps extending up to about 2,370 Km^2 [24]. About 50% of this area is enclosed with water which is about 55% of Nigerian freshwater swamps [25, 26]. Uluocha and Okeke noted that the Niger Delta area of Nigeria is among the ten highly significant wetlands and marine environment of the world [27], because of its ecological biodiversity the area is seen as one of the world's richest wetlands in terms of biodiversity [28].

The first discovery of crude oil in Nigeria at Oloibiri now in Bayelsa State a part of Niger Delta by Royal Dutch Shell [29,30], and now in several other parts of the Niger Delta, has created a lot of environmental problems including destruction of the wetlands resulting from crude oil pollution [31]. Though the oil industry in this region has imparted significantly to the economic growth of the country, the activities of the oil industries in this area has negatively affected its ecosystem [32]. It has been reported that over the last 50 years about 9-13 million barrels of crude oil has been spilled in the Niger Delta area which is equivalent to 50 Exxon Valdez spills [33].

This research work therefore is intended to investigate the effectiveness of cow lumen and NKP fertilizers in enhancing the remediation of crude oil polluted freshwater wetland and the effect on the physiochemical properties of the soil.

MATERIALS AND METHODS

Study site The study was conducted at the back-gate of Imo State University Owerri, Imo State Nigeria, which lies within the coordinates; latitude 5.498229°N and longitude 7.044206°E at 68.5m above sea level. Imo State being a part of Niger Delta area is classified in the tropical rain forest zone with ecosystem comprising of diverse species of flora and fauna both aquatic and terrestrial species [34]. The site is where Lake Nwaebere empties. Hence it was chosen to represent fresh water wetland. Though Imo State is an oil producing state but there is no record of crude oil pollution in this area unless caused by runoff from polluted surroundings resulting from anthropogenic activities.

The crude oil used for the experiment was procured from Nigerian Agip Oil Company located at Ebocha, River State, Nigeria. NPK 20:10:10 fertilizer was purchased from Imo State ADP way house at Egbu Road Owerri lmo State, Nigeria. Cow lumen (offals) was obtained from the slaughter house located behind Somachi Park, Egbu Road Owerri. The chemicals used for the analysis were procured from Finlab, Owerri, which were of analytical grade.

Experimental design The plot of land for the experiment was cleared and allowed to stabilize for three days. Then, a bed of about 50cm x 50cm x10cm each was prepared on it to form a randomized complete block design of 5 beds in a row. Enough space was provided between beds to create access to the experimental site during sample collection and tilling of the site as well as to check leaching effect of the crude oil in the plots [35].

The site was given five different treatments one or more on each plot. The plot which was divided into five beds in one rows were treated as follows: plot A was unpolluted while plot B, C, D and E, were polluted with equal volume of crude oil (2L) using sprinkler. Plots A and B served as the control. The treated plots were tilled twice a week with shovel to provide aeration and mixing of the applied nutrients with the contaminated soil [36]. The treatment given to each block is as shown in fig.1. There was no need to water the plots since the experiment was conducted in the open environment within the months of June and July, 2012, for sixty days when the onset of rainfall was high.

A	B	C	D	E
Unpolluted soil	Crude oil polluted soil	Polluted soil + 10kg NPK	Polluted soil + 10g cow lumen	Polluted soil + 10kg cow lumen + 10kg NPK

Fig. 1: Randomized block design

Soil Sampling Soil sample was collected using a soil auger that was thoroughly washed and dried. Soil samples were randomly collected at two different depths of 0-5cm and 10-15cm. Five sampling points were used in each of the plot (ABCDE). Samples collected from each block were deposited into a black polythene bags and labeled properly with masking tape. The samples for the total petroleum hydrocarbon (TPH) measurements were placed in glass bottles and sealed with aluminium foil [36]. In the laboratory soil sample collected from a particular block (i.e. A or B) were mixed together to form a homogeneous sample. The soil samples were air dried at room temperature and sieved through a 2mm mesh.

Sample analysis Parameters analyzed in the soil samples were pH, electrical conductivity (E.C), phosphate, PO^{3-}_4, available phosphorous, P, % organic carbon, % total nitrogen N, carbon/nitrogen ratio and total petroleum hydrocarbon, TPH. The electrical conductivity of the soil was determined with Hanna conductivity meter Hi98303 while pH was measured using Hanna pH meter Hi98107. Phosphate was extracted in the soil using 0.5M sodium bicarbonate at soil-water ratio of 1:50. The extracted phosphate was reacted with phosphate reagent (2) on the reducing condition to form a blue colour complex. The phosphate and available phosphorous were then determined in the sample using multiparameter bench photometer (HANNA H1832007). Organic-carbon content was determined by the wet combustion method of Walkey and Black [37], while the total nitrogen was determined as described by Van Reeuwijk [38]. Total Petroleum Hydrocarbon (TPH) was determined with 2.5g of the sample which was added to 10ml of hexane and 2.5g of dried sodium sulphate, this was shaken vigorously in Teflon seal screw cap for 30 minutes on a shaker, then extracted solvent was allowed to settle down properly before decanting as described by Ilori et al.[39]. After zeroing with pure hexane solvent as blank, the absorbance of the extracts was measured at 420nm using UV/visible spectrophotometer (UV-spectrolab752). A standard curve was plotted with absorbance of the crude oil dissolved in hexane. TPH was then quantified by a plot of concentration of the soil extract against the absorbance and concentration of the unknown extract determined by conversion of the absorbance to concentration using the Eq. (1) [39].

$$TPH\ (\text{mg/kg}) = \frac{Absorbance\ x\ CF\ x\ DF\ x\ EV}{weight\ of\ soil\ sample} \quad (1)$$

Where CF = conversion factor from absorbance to mg/l extract, DF = dilution factor, EV = extracted volume of solvent (L)

RESULT AND DISCUSSION

The results of the soil characteristics after fifteen days and the sixty days of remediation are presented on table 1 to 2 and fig. 2 to 9. The result indicates that the pH ranged from 5.32 – 7.03 as shown in figure 2. The pH values of B,C,D and E were more elevated than that of A which was unpolluted, and received no treatment. The pH at the end of sixty day of remediation was lower when compared with the values after fifteen days of remediation as shown on table 1 and 2. The observation is comparable with earlier reports [36,40,41,42]. Changes in pH level due to crude oil contamination could alter the soil fertility as well as other physiochemical properties which may as well influence the solubility and availability of soil nutrients [43,44]. The pH of the plots are in the order B > D > C > E > A after fifteen days, and E > C > D > B > A at the end of sixty days.

The electrical conductivity ranged from 35.30 – 83.54 µS/cm. Also there was an increase in the E.C of the soil in the plots even after fifteen days of pollution and remediation when compared with plot A and B that was unpolluted and untreated respectively. The increase in the E.C could be attributed to introduction of the crude oil and subsequent addition of the fertilizer to the plots. A similar observation on the changes in the E.C. of crude oil contaminated soil has been reported [45].

Table 1: Physiochemical properties of the soil after 15 days of remediation

Plots	pH	E.C µS/cm	PO^{3-}_4 mg/kg	P mg/kg	Organic C %	Total N %	C/N	TPH mg/kg
A	5.32	35.30	21.80	6.62	0.15	0.27	0.56	42.05
B	5.96	46.14	11.57	5.02	0.41	0.17	2.41	690.45
C	5.65	83.54	13.38	5.67	0.45	0.20	2.25	582.12
D	5.76	83.38	12.63	5.67	0.42	0.19	2.21	595.23
E	5.57	82.05	13.75	6.04	0.39	0.22	1.77	467.18

Table 2: Physiochemical properties of the soil after 60 days of remediation

Plots	pH	E.C µS/cm	PO^{3-}_4 mg/kg	P mg/kg	Organic C %	Total N %	C/N	TPH mg/kg
A	5.37	35.70	21.82	6.54	0.14	0.28	0.50	42.10
B	5.86	48.31	11.53	5.25	0.40	0.14	2.22	733.03
C	7.03	56.24	14.76	5.86	0.38	0.18	2.11	511.24
D	6.74	73.68	13.57	5.43	0.34	0.16	2.13	532.13
E	6.98	48.05	15.05	6.23	0.32	0.20	1.60	317.56

The results indicate slight differences in the soil phosphate as shown on table 1 – 2 and fig.4, the values ranged from 11.53 – 21.83 mg/kg. The unpolluted and the polluted plots which were remediated had higher phosphate level than the polluted plot which was not remediated

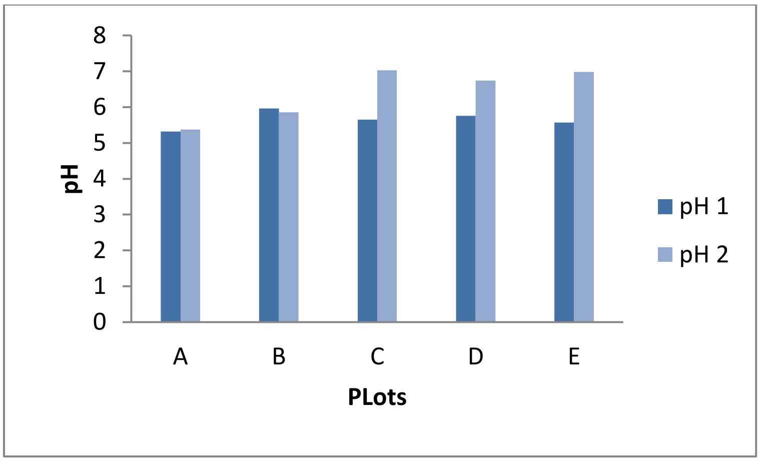

Fig. 2: pH of the soil after 15 days (1) and 60 days (2)

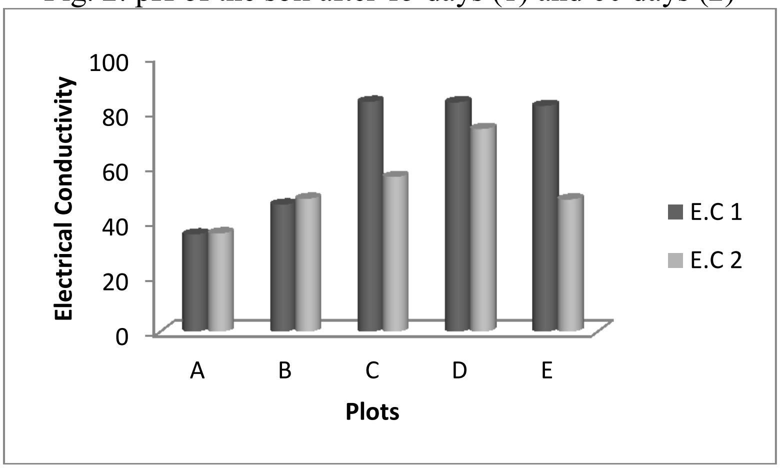

Fig. 3: E. C of the soil after 15 days (1) and 60 days(2)

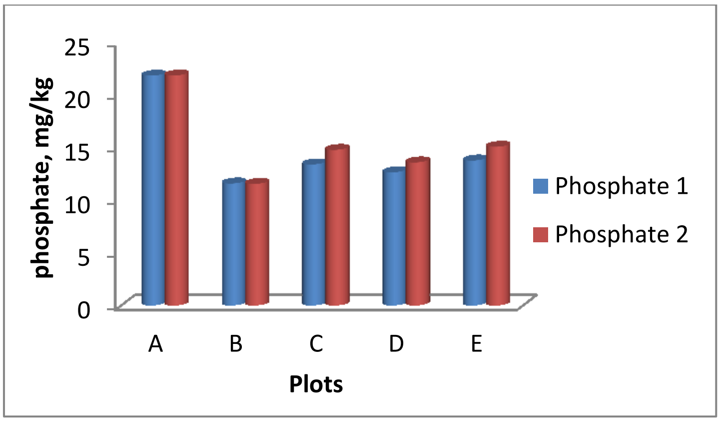

Fig. 4: Phosphate level of the soil after 15 days (1) and 60 days (2)

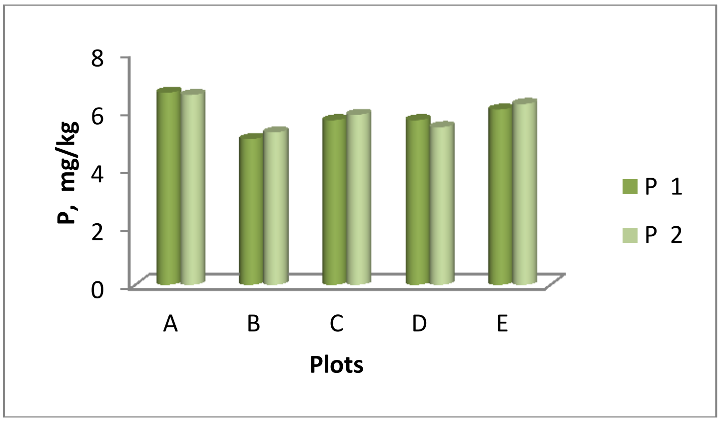

Fig. 5: Available phosphorous of the soil after 15 days (1) and 60 days (2)

The highest level of phosphate was observed in the unpolluted plot which received no treatment, however, the polluted plots which were treated with either organic, inorganic fertilizer or a combination of the two showed higher phosphate level than the unremediated plot. The phosphate values after fifteen days are in the other A > E > C > D > B, while the order after sixty days is A > E > C > D > B. A similar observation has been reported in a related study [46].

Similarly, the available phosphorous level was least in the polluted plot which was not remediated, while the difference between the plot that received combined treatment and the unpolluted plot is not significant as shown in fig. 5. The values ranged from 5.02 – 6.62 mg/kg, and the order is A > E > C > D > B after fifteen days and sixty days.

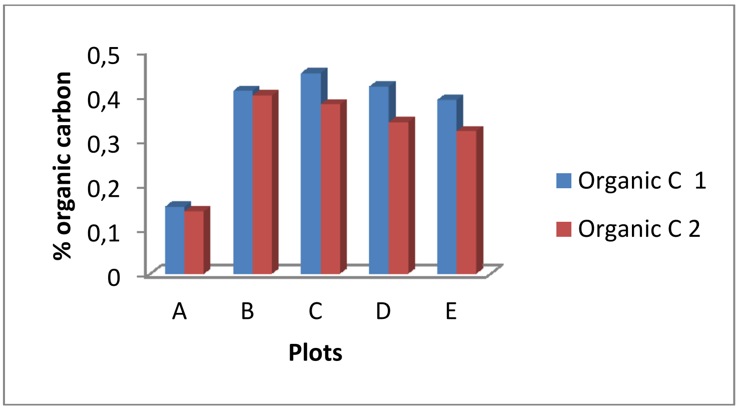

Fig. 6: % organic carbon of the soil after 15 days (1) and 60 days (2)

There is an observable increase in the organic carbon content of the soil as shown in fig.6. The organic carbon content of the soil in plot A which was not polluted with crude oil was the least as shown in fig. 6, this could be attributed to the pollution of the soil in plot B to E by crude oil which elevated the carbon content of the plots, this observation has been substantiated by earlier reports [47,48,49]. The organic carbon content at the end of remediation treatment reduced significantly

Also, the percentage total nitrogen content of the plots showed marked difference between the values after fifteen days and sixty days of remediation when compared with plot A as shown in fig.7. The percentage total nitrogen values ranged from 0.14 – 0.28 %. The highest value was observed in the unpolluted plot (A), while the lowest value was shown by plot B,

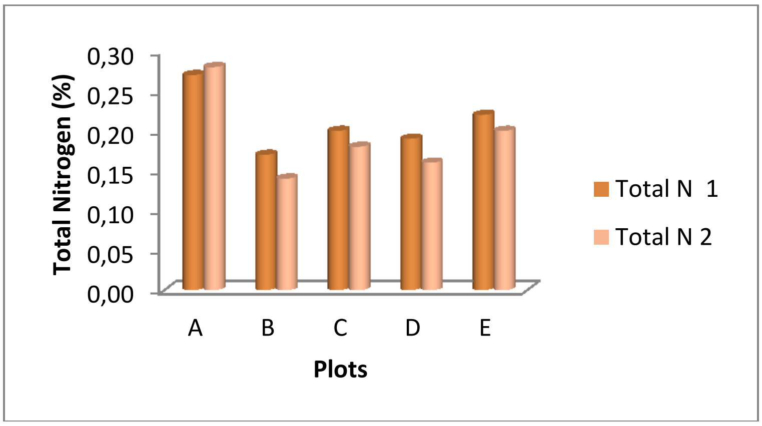

Fig. 7: % Total Nitrogen of the soil after 15 days (1) and 60 days (2)

which never received any treatment? On the other hand among the treated plots, plot E which was given combined treatment had the highest value of %N as shown in fig.7 at the end of the remediation. There was also an observable decrease in the nitrogen content of the plots after fifteen days and sixty days. This implies that there is a reduction in the nitrogen content at the end of remediation regardless of the added nutrients, which could be attributed to utilization by microorganisms for the degradation of the hydrocarbons [50]. A similar observation has been reported in related studies [51,52].

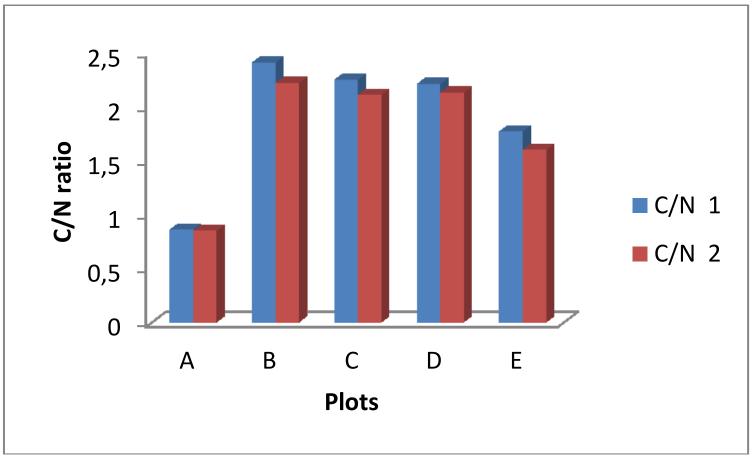

Fig. 8: C/N of the soil after 15 days (1) and 60 days (2)

The results as shown in fig.8 indicate that there was an increase in the nitrogen carbon ratio of the plots after crude oil contamination, this however reduced significantly with the application of remediation treatments. The result is in the order A < E < C < D < B, for both after fifteen days and sixty days of remediation. The highest level of reduction was observed in plot E which was treated with both inorganic and organic fertilizers indicating higher efficacy in remediating crude oil polluted fresh water wet land. The results obtained in this study are comparable with that earlier reported [36,51,52,53].

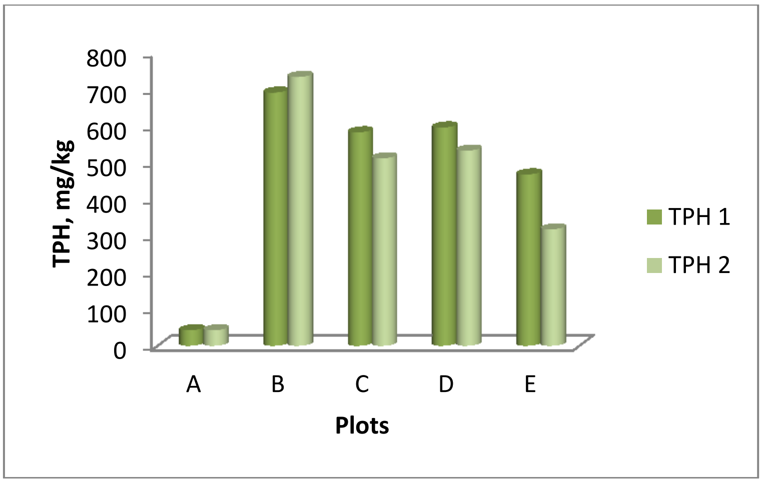

Fig. 9: TPH of the soil after 15 days (1) and 60 days (2)

There was a marked significant increase in TPH concentration in plots B, C, D and E when compared with plot A, this eventually was reduced in plots C, D and E which were remediated. The TPH content of the plots ranged from 42.05 – 733.03 mg/kg. At the end of sixty day of treatment the TPH content in the treated plots were reduced according to the order E < C < D < B. Again, the least value was observed in plot E which received combined treatment with organic and inorganic treatments followed by plot C that was treated with inorganic remediating agent. This indicates that the combination of cow lumen and NPK fertilizer were more effective in accelerating the rate of hydrocarbon degradation than the use of single remediating agent in this study. The report of this study agrees with Tanee and Kinako's submission that there was significant reduction in the THC of crude oil contaminated soil remediated with a combination of organic and inorganic fertilizer [53].

CONCLUSION

It could be observed from the study that crude oil pollution of wetland may negatively affect physiochemical properties of the soil. Results of the study indicates that remediation of crude oil polluted fresh water wetland could be achieved with the use of organic and inorganic fertilizer like NPK and cow lumen to a reasonable extent. A combination of organic and inorganic fertilizer proved to be more efficient in stimulating the degradation of the petroleum hydrocarbon as most of the physiochemical properties observed in this study were improved when compared with that of the untreated plots.

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