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Examining and Developing a Model of Soil Degradation Pattern for Total Petroleum Hydrocarbons (TPH) in Biocell in Ogoniland, Rivers State, Nigeria

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Abstract

The study examined and developed a model for soil degradation pattern of total petroleum hydrocarbons in biocell in Ogoniland, Rivers State, Nigeria. The study involved collating soil sample baseline data in line with the total petroleum hydrocarbon (TPH) contamination level at different depths of the soil lithography. The baseline data was obtained through initial sampling of the soil contaminant level at various depths of the site. The site was sectioned according to the level of contamination to be excavated for treatment. The key performance indicator for the study was TPH value, therefore analysis was done only on TPH value. The soil in the biocell was segmented into 4 sections for sampling. TPH is the total concentration of all hydrocarbons eluting from n-nonane to n-hexatriacontane, excluding target PAH Analytes. TPH is the total of the aliphatic hydrocarbons (C9–C18), the aromatic hydrocarbons (C11–C22), and the aliphatic hydrocarbons (C19–C36). The samples were documented in a chain of custody and sent to the laboratory for further analysis. Descriptive statistics in Matlab were used for data analysis. Findings showed that the TPH degradation within the biocell from day 0-21, was in proportion to the number of days after treatment was applied in the biocell and the level of contaminant was significantly reduced to below target value of 50mg/kg after each treatment cycle. A treatment cycle starts when the contaminated soil is spread in the biocell to when the results show that the target value is achieved. The study concluded that the effectiveness of the pollution management system as processed within the biocell was assessed in terms of TPH reduction in the contaminated soil. It was observed that there was a significant reduction in all treatment sites as seen in the degradation curves. It is recommended that any best practice will require a good plan before actual execution; this can be achieved with a prediction tool that gives knowledge and direction of flow with a predictive tool.

Keywords: Model; Soil; Degradation; Total petroleum hydrocarbons; Biocell

Introduction

Oil spills due to blowouts, leakage from pipelines, vehicles, tanks or storage areas, service areas, accidents, and dumping of waste petroleum products lead to higher levels of petroleum hydrocarbons in soil. These significantly deteriorate the quality of soil and render it unsuitable for intended use. The potential hydrocarbon-contaminated sites are fuel filling stations, distribution depots, oil production, refineries and associated industries, garages, the automotive industry, haulage yards, the scrap metal industry, airports, the aerospace industry, waste processing, and disposal sites. The extent of soil pollution by petroleum products and oil sludge has affected millions of cubic meters (Zukauskaite *et al.*, 2008). According to Riser Roberts (1998), hydrocarbons in the soil are considered toxic when they reach concentrations greater than 100 µg g-1 soil.

PHC contamination in soil is a concern for several reasons: (i) the chemically reactive nature and volatility of PHC that can pose a fire or explosion hazard, especially if vapors enter confined spaces; (ii) most PHC constituents are toxic to some degree; (iii) lighter hydrocarbons (i.e. those of lower molecular weights) are mobile and can become a problem at considerable distances from their point of release due to transport in the ground, water or air; (iv) larger and branched-chain hydrocarbons are persistent in the environment; (v) PHC may create aesthetic problems such as offensive odor, taste or appearance in environmental media; and (vi) under some conditions, PHC can degrade soil quality by interfering with water retention and transmission, and with nutrient supplies.

The contamination of the natural environment by petroleum-derived substances contributes to the degradation of land (Sztompka, 1999). Contamination of soil with petroleum-derived substances creates some changes in the soil's biological composition. This can lead to water and oxygen deficits as well as to a shortage of available forms of nitrogen and phosphorus (Wyszkowska et al., 2001). According to Wyszkowski, *et al.*, (2002), pollution of the soil environment with petroleum and refinery products is one of the factors expressing anthropopression (more disturbances due to human action). Oil pollution prevents normal oxygen exchange between the soil and the atmosphere due to the hydrophobic properties of the oil (Atlas, 1977). It also inhibits seed germination and plant growth (Hazel, 2005; Odjegba & Sadiq, 2002). Al-Ashen *et al.*, (1999) explained that hydrocarbon contamination exerts an adverse effect on soil conditions such as higher acidity, reduced carbon, nitrogen, phosphorus, exchangeable cations availability, and depressed microbial activity.

Terrestrial PHC contamination can have detrimental effects on the biological, physical, and chemical properties of the soil. Refined petroleum products such as diesel fuel, aviation fuel, and gasoline are complex mixtures of compounds with toxicity dependent on the composition of the fuel and the percentage of each constituent. Some compounds are carcinogenic, mutagenic, or toxic to humans, animals, plants, and microorganisms (Yang *et al.*, 2009). Petroleum compounds like gasoline, diesel, motor oil, etc. are largely responsible for the changed fertility of the soil (Iwanow *et al.*, 1994). Biological activity may be lost in the soil polluted by petroleum-based products and could not be able to recover over ten years (Wyszkowska *et al.*, 2001). Like other petroleum products, diesel oil also hurts the biochemical and physicochemical characteristics of soils (Wyszkowska *et al.*, 2002). Since the petroleum hydrocarbons and other toxic compounds from used motor oil are a major threat to soil biota and soil health, used motor oil is deemed to cause soil quality decline. When it enters the soil, it alters some of its properties resulting in poor aeration in soil, immobilization of soil nutrients, and lowering of soil pH. These modifications of the physicochemical properties in the soil lead to changes in the biological composition of soil habitats, causing mass mortality of the animals living in the topmost layers of soil resulting in a rapid increase in the organic matter of the soil; finally disrupting the biological equilibrium of soil (Atuanya, 1987).

Accidental leakages during hydrocarbon fuel transportation and other activities are inevitable, making these hydrocarbons the most common global environmental pollutants (Ganesh & Lin, 2009). Petroleum hydrocarbons cause soil and sediment contamination, which is a serious ecological problem since the soil that has been contaminated by mineral oil products can be potentially a risk to environmental media surrounding the affected area. This is due to the further

distribution of these chemicals in the environment, such as dissolution in groundwater and subsequently in drinking water, evaporation into the air, plant uptake, and other processes.
Therefore, to prevent the spreading of mineral oil pollutants, the soil must be remediated. The removal of oil relates to microbial degradation (Groudeva *et al.*, 2001). Hydrocarbons persist for months and even years following major oil spills, indicating that hydrocarbon biodegradation is slow in most natural environments (Bento *et al.,* 2005).
In the past, innovative remedial technologies were limited. Recently, several approaches have been employed globally to reclaim contaminated soils, of which bioremediation or biodegradation is one of the most important methods. Bioremediation is the use of microorganisms' consortia or microbial processes to degrade and detoxify environmental contaminants (Margesin *et al.,* 2007; Singh *et al.*, 2008; Zhao & Poh, 2008). It is a new technology that derives its scientific justification from the emerging concept of Green Chemistry and Green Engineering. It is a fast-growing promising remediation technique increasingly being studied and applied for pollutant clean-up.
Most of the advances in bioremediation have been realized through the assistance of the scientific areas of microbiology, biochemistry, molecular biology, analytical chemistry, and chemical, and environmental engineering, among others. These different fields, each with its approach, have actively contributed to the development of bioremediation progress in recent years.
In bioremediation, bacteria that feed on hydrocarbons and transform them into carbon dioxide can be applied to an affected area. Bioremediation is a rapidly developing field of environmental restoration that utilizes natural activity to reduce the concentration and toxicity of various hazardous substances, such as petroleum products, aliphatic and aromatic hydrocarbon (including polyaromatic hydrocarbons and polychlorinated biphenyls), industrial solvents (phenols, benzene, acetone, etc.), battery liquids, pesticides, and heavy metals into less toxic or nontoxic substances to environmentally safe levels (Korda *et al.,* 1997). Approaches or techniques in petroleum hydrocarbon biodegradation and the microbial community involved in the hydrocarbon bioremediation processes are reviewed below.
The systematic use of biological processes in the design of engineered environmental remediation systems is today well-developed and documented (Lehr, 2004). Contemporary environmental biotechnology utilizes techniques that employ usually natural strains of microorganisms to mobilize and remove organic or immobilize inorganic pollutants from the environment. The key advantage of bioremediation processes as compared to other biological technologies is that they can employ enzymatic metabolic pathways that have evolved in nature over very long periods, thus becoming very specific. The combination of such pathways can make possible the degradation of a wide variety of hazardous pollutants. In recent times, metabolic pathways for the degradation of compounds previously considered non-degradable have been identified (Alvarez & Illman 2006). Laboratory and field techniques for assessing the applicability of biological processes for the degradation of the pollutants that are present at specific sites have become available (Beek, 2001; Neilson *and Allard*, 2008).
Monitoring of TPH in soil is very essential in line with fit-for-purpose practice; this justified the focus of the present study. Thus, the study examined and developed a model for soil degradation pattern of total petroleum hydrocarbons (TPH) in biocell in Ogoniland, Rivers State, Nigeria.

Materials and Methods

The study was carried out in Eleme, Gokana, Khana, and Tail LGAs of Rivers State, in the Niger Delta region of Nigeria (Figure 1). The Eleme site is located at Nkeleoken- Alode (291069E ; 527211N). The site lies along the SPDC pipeline right of way. The location of site in Gokana LGA was at Debon Eastings: Northings 309033: 512950 308999: 512951 309030: 512870 309067: 512889 308998: 512909 along the 24" SPDC Pipeline. The site in Tai LGA was located at Buemene in Korokoro community, Tal LGA with geo-reference: Eastings: 311740, Nothings:

524213 which was around the SPDC WELL 05 location. The site in Khana LGA was located at Kpean community in Khana LGA with Geo-reference: Eastings: 330095, Nothings: 509149; within the SPDC Well 013.

TPH degradation involved collating soil sample baseline data in line with the total petroleum hydrocarbon (TPH) contamination level at different depths of the soil lithography. The baseline data was obtained through initial sampling of the soil contaminant level at various depths of the site. The site was sectioned according to the level of contamination to be excavated for treatment. The key performance indicator for the study is TPH value, therefore analysis was done only on TPH value. The soil in the biocell was segmented into 4 sections for sampling. Each section was divided into 5 sub-sections and grab samples were collected from each sub-section and homogenised as one sample. The samples were collected in amber glass bottles and put in coolers with cooling packs to about 4 degrees Celsius. A glass bottle was used as plastic will react with the organic components within the soil. The samples were documented in a chain of custody and sent to the laboratory for further analysis. The parameter of concern in this study is the total petroleum hydrocarbons (TPH). TPH is the total concentration of all hydrocarbons eluting from n-nonane to n-hexatriacontane, excluding target PAH Analytes. TPH is the total of the aliphatic hydrocarbons (C9–C18), the aromatic hydrocarbons (C11–C22), and the aliphatic hydrocarbons (C19–C36). Descriptive statistics in Matlab were used for data analysis.

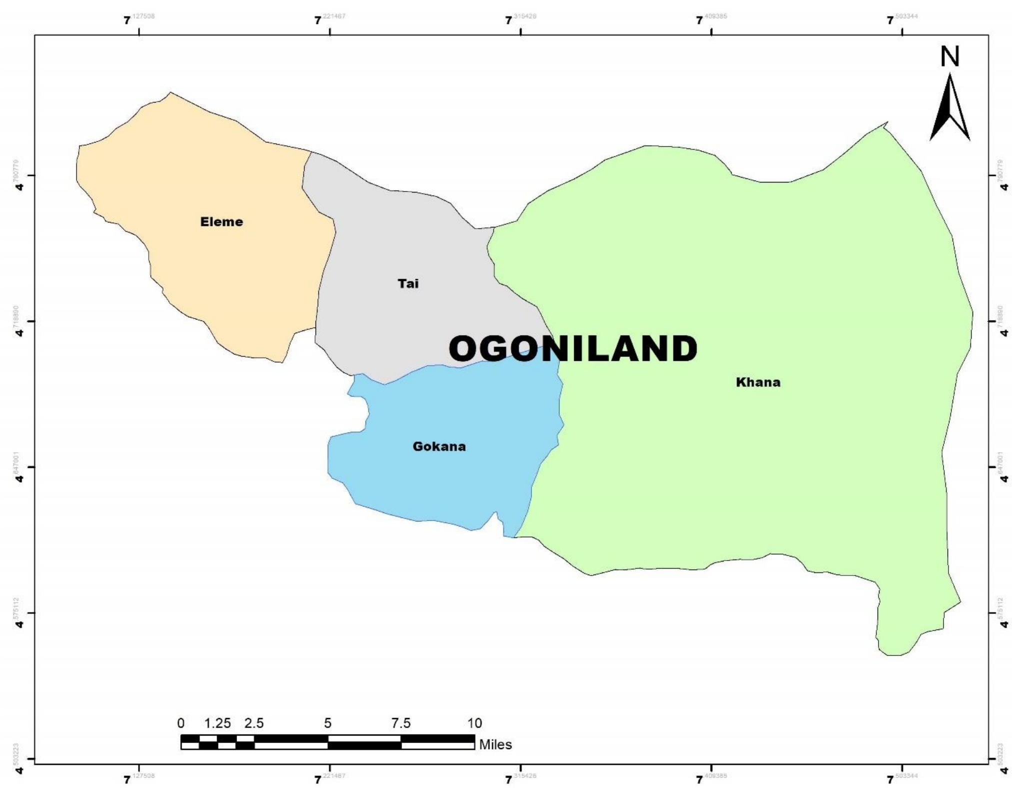

Figure 1: The LGAs in Ogoniland on the Map of Rivers State

Source: Source: ArcMap 10.7.1

Results and Discussions

The results in the graphs below show values of residual TPH within the biocell at the different study areas. Each graph represents the level of hydrocarbon degradation within a particular treatment cycle ranging from 0-21 days.

Fig.1-4 (a-b), shows the residual TPH and degradation pattern in the study sites. The chart was plotted with the residual TPH values on the vertical axis against the number of days after remediation (on the horizontal axis), in the biocell. The chart also shows the error bars that give an average measurement of the figures in consideration of the margin of error.

Fig. 5-8 also shows a similar behavioral pattern of the hydrocarbon contaminants in the biocell days after treatment in all treatment areas of the study. It was observed that the TPH degradation within the biocell from day 0-21, was in proportion to the number of days after treatment was applied in the biocell and the contaminant level was significantly reduced to below the target value after each treatment cycle.

Table 4 shows the TPH values of the contaminated soil at various stages of treatment. For each treatment cell, the volume of soil and initial TPH value was constant in all the study sites excavated at specific depths. TPH values were recorded every 7 days to evaluate the effectiveness of the process and it was observed that there was a significant reduction in contaminant level as shown in the results in Table 4 in line with the number of days.

The effectiveness of the pollution management system as processed within the biocell was assessed in terms of TPH reduction in the contaminated soil. It was observed that there was a significant reduction in all treatment sites as seen in the degradation curves below. All treatment areas show the variation in the residual TPH concentrations days after remediation with enhanced treatment. Despite the all-too-common features in all the treatment areas, little spikes are seen in the TPH in some treatment areas, specifically in the Khana treatment area. This is due to the non-homogenous mixing of the treated soil and inundation of the biocell by rainwater, resulting in poor aeration and retention of treatment compounds. However, the overall result of the treatment as seen on the degradation curve shows the effectiveness of the process in the biocell.

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Figure 1: Eleme Treatment Area

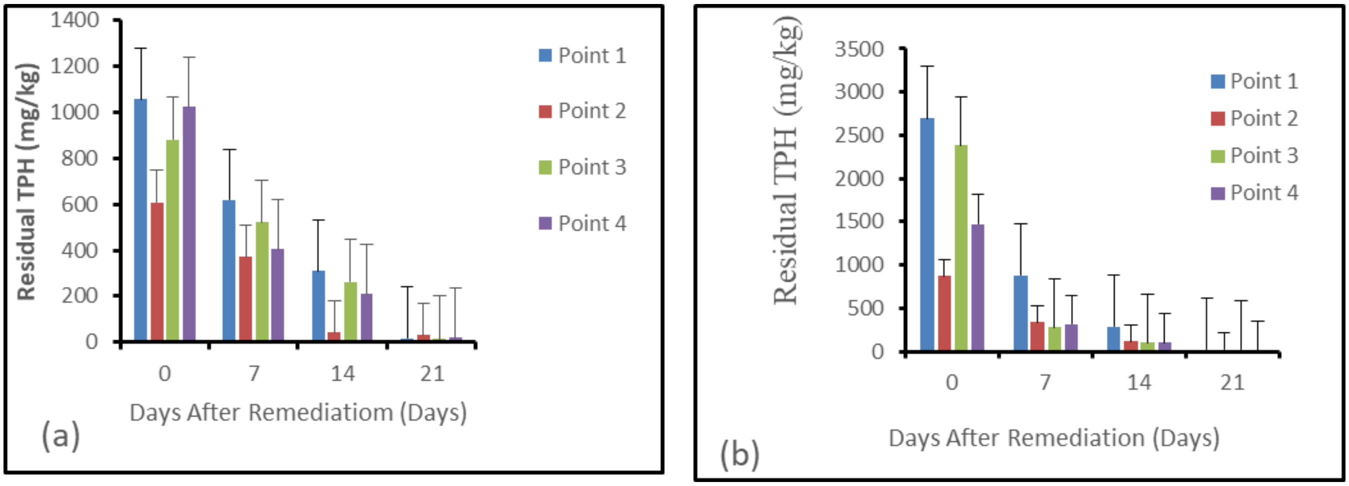

Figure 2: Gokana Treatment Area

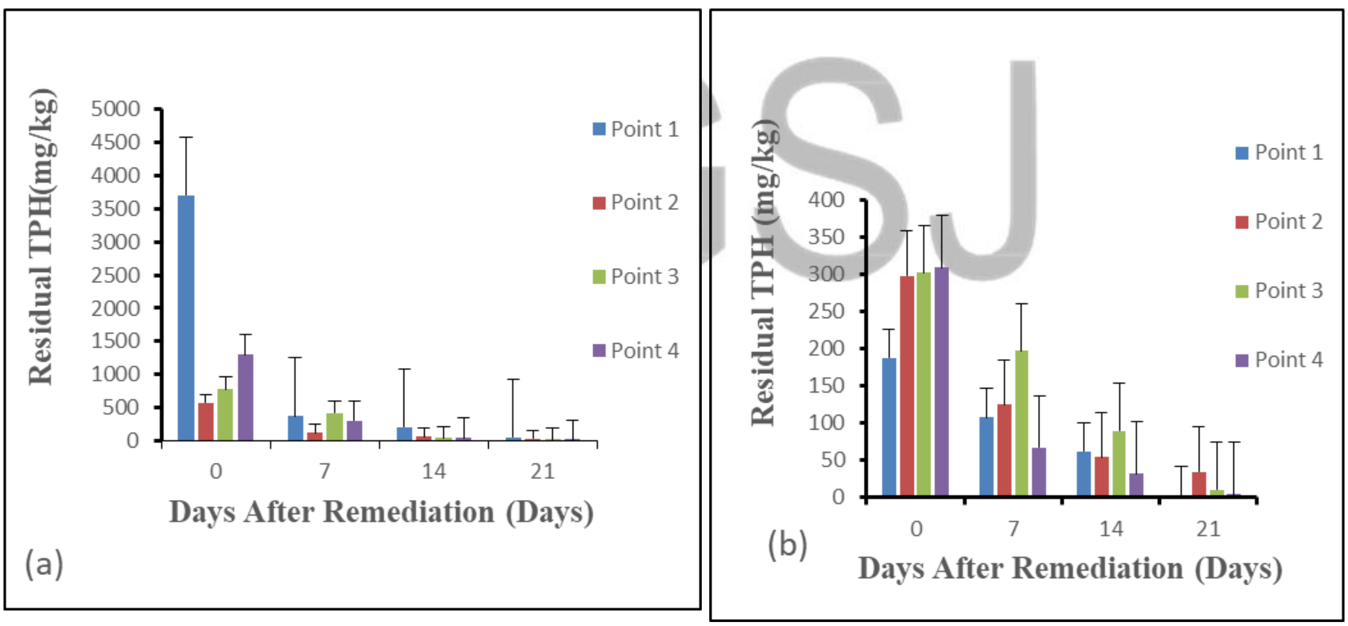

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Figure 3: Tai Treatment Area

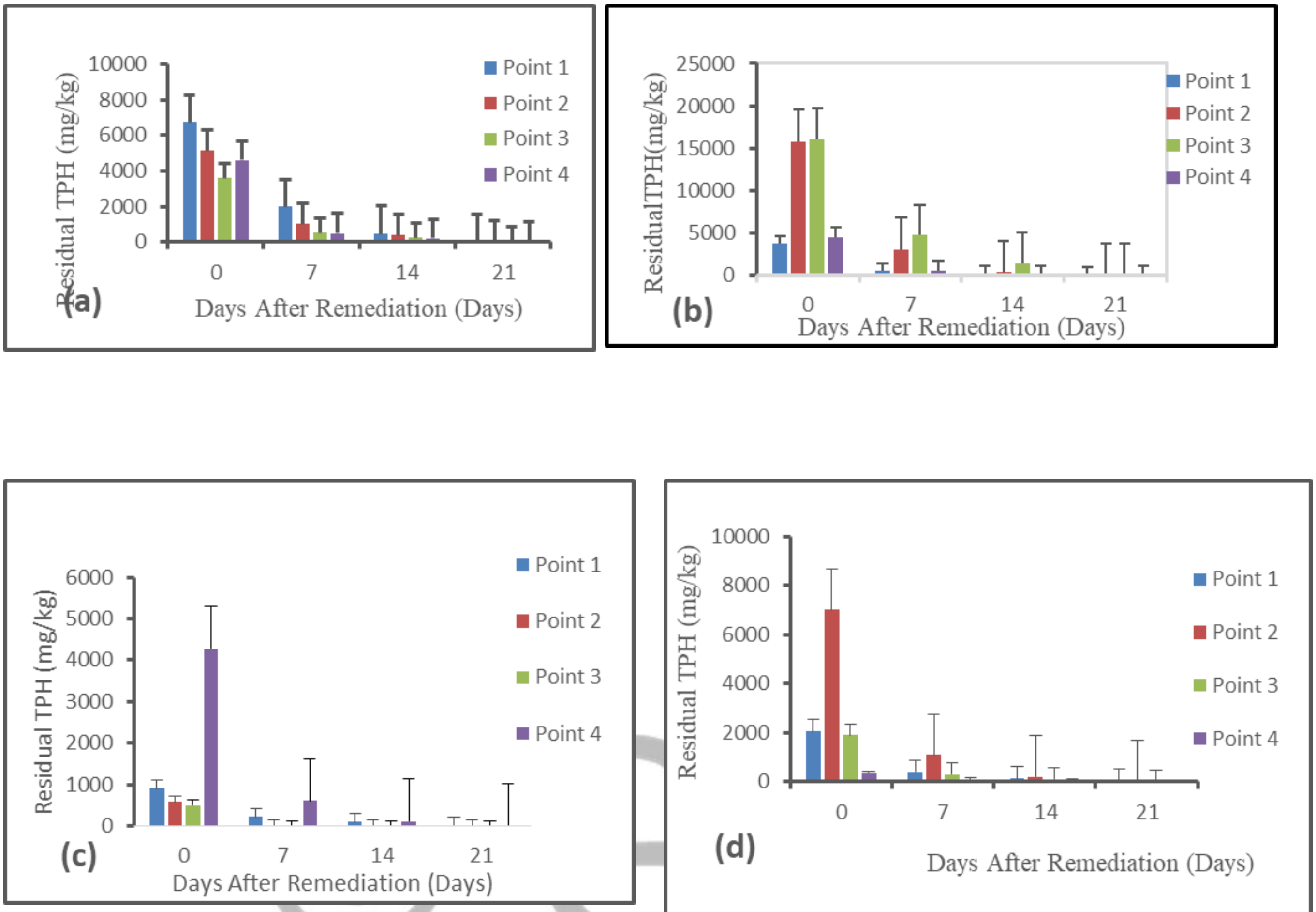


Figure 4: Khana Treatment Area

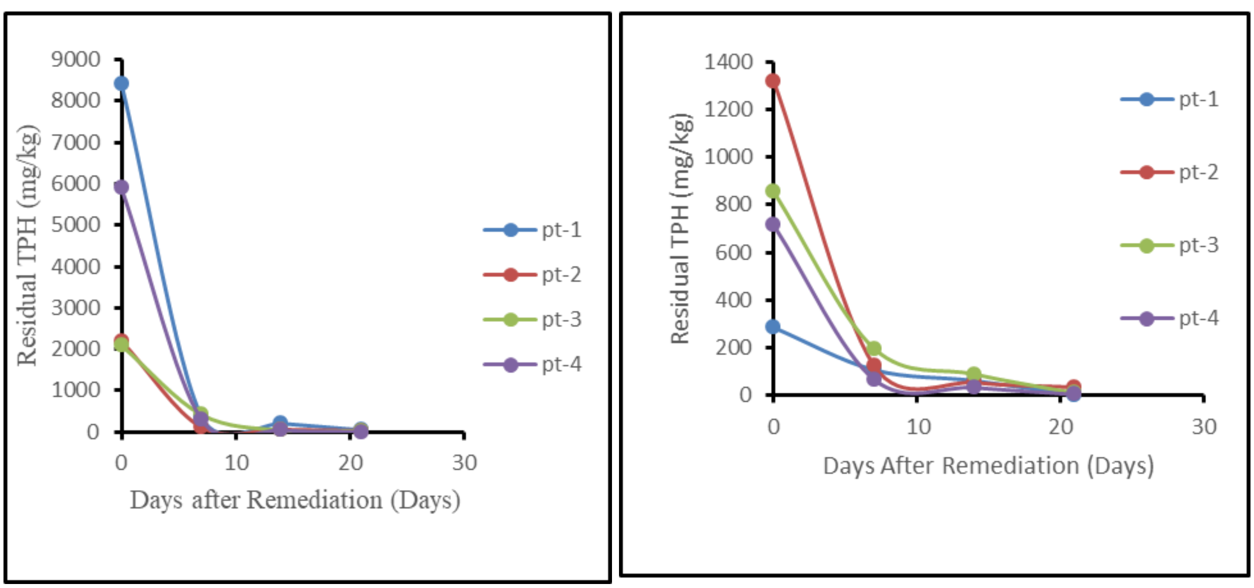


Figure 5: Degradation curve for Eleme Treatment Area

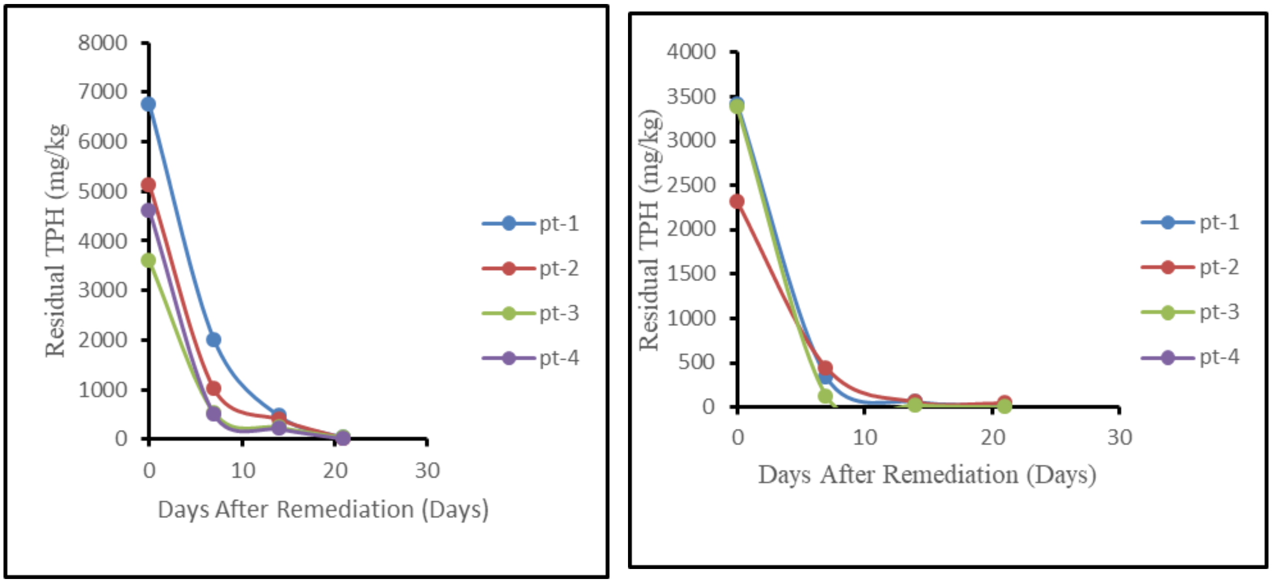


Figure 6: Degradation curve for Gokana Treatment Area

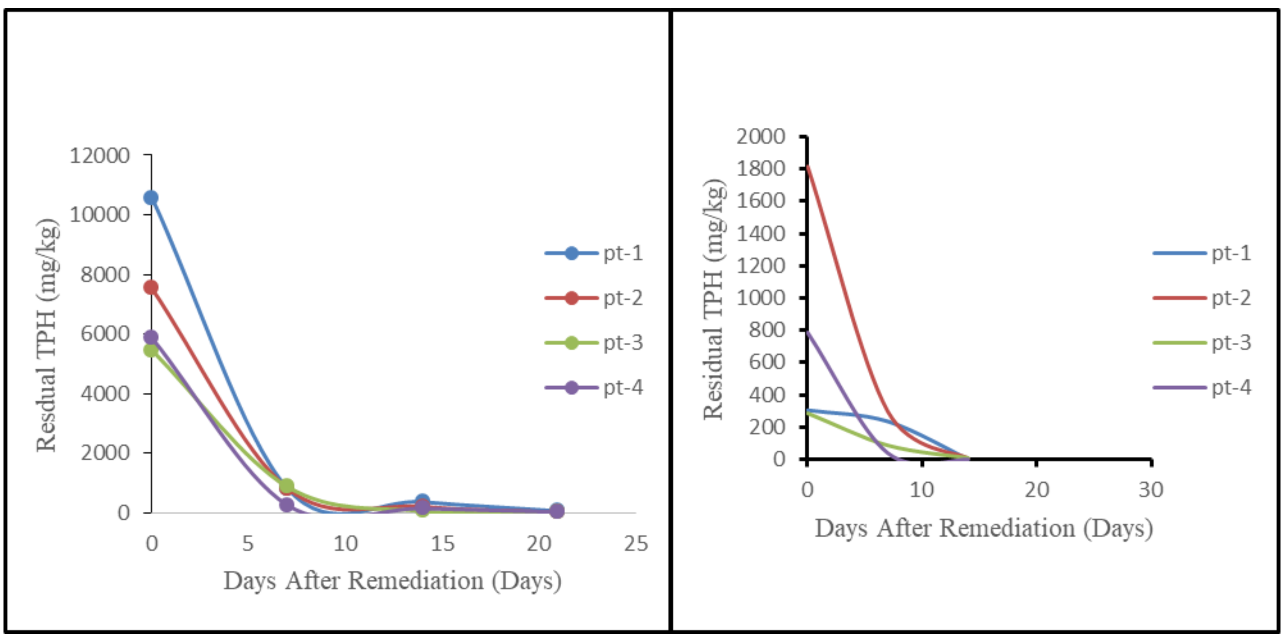
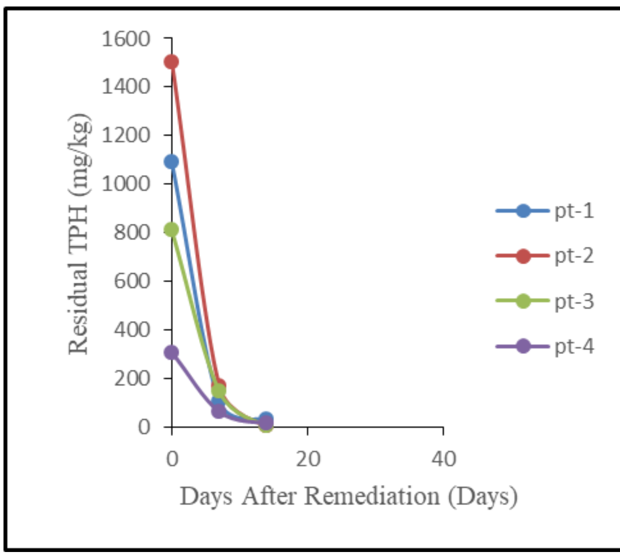
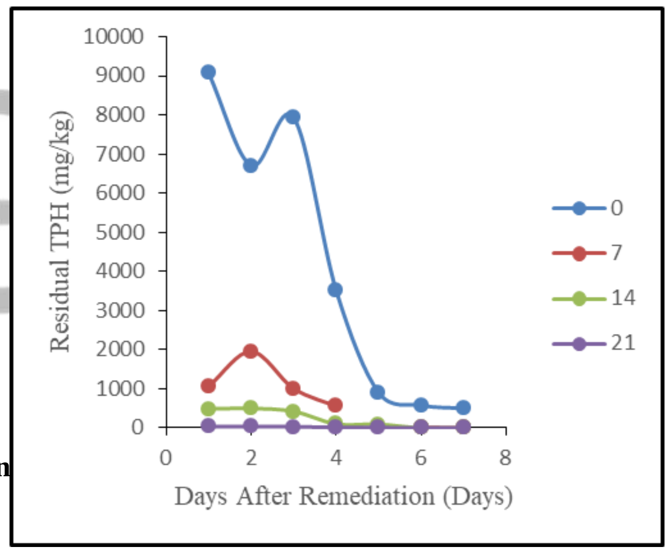


Figure 7: Degradation curve for Tai Treatment Area





TPH regression model

Statistical analysis was carried out to show the effectiveness of treating contaminated soil within the biocell as an engineered treatment system for oil-contaminated soil in the study area using Matlab software as shown in section. One-way analysis of variance (ANOVA) was used to analyze data on soil properties, with treatments and incubation period as the main components. For entirely randomized designs, statistical significance was accepted at a P0.05 confidence level.

The change in TPH value over three weeks was examined using a balanced one-way ANOVA in all study areas. Data stored from analytical results was extracted using Matlab codes. ANOVA was used to test change in TPH for control and treatments. For all ANOVAs, a significant value was obtained, In hypothesis testing with its two levels, independent means that were statistically distinct from one another were found. To guarantee proper interpretations of the tests on main effect hypotheses, all suitable interactions between the various treatment cells, soil depth, and treatment were also investigated.

The mathematical link was determined using multiple linear regression (MLR) between the rate of TPH removal concerning days, and treatment, at each study area. The independent factors (TPH before treatment and TPH after treatment) and the knowledge of the various factors were utilized to accurately anticipate the degree of influence they have on the outcome variable after it had been established that they can predict the dependent variable (number of days). The model generated a connection that best approximates each of the individual data points as a straight line (linear) graph as shown in Fig 9 (a-d) for all treatment areas.

From the Matlab code, the F-calculated was compared with F-tabulated in APP B to get the significant difference for each treatment cell, and the overall data was combined and analyzed in Matlab to produce an equation for each treatment area that can be used to predict the rate of degradation of a contaminated site within the study area, with a known value of the initial TPH and inputting a certain number of day as shown in the equation below for the four study area.

$$tph = 1428.575 - 126.0344 * d + 0.1312 * tph0 \quad (1)\ \text{Eleme}$$

$$tph = 176.9184 - 13.0145 * d + 0.0505 * tph0 \quad (2)\ \text{Gokana}$$

$$tph = 949.4556 - 105.0917 * d + 0.2301 * tph0 \quad (3)\ \text{Tai}$$

$$tph = 622.7742 - 58.6622 * d + 0.1554 * tph0 \quad (4)\ \text{Khana}$$

Using multiple regression as shown in Equation 1 – 4, it was observed that the initial TPH value affects the value of TPH that occurred in the individual days. Therefore, a regression equation derived is expressed as a function of days (d) and initial TPH value (tph0). The higher the TPH value before treatment determines the number of days it will take for complete treatment.

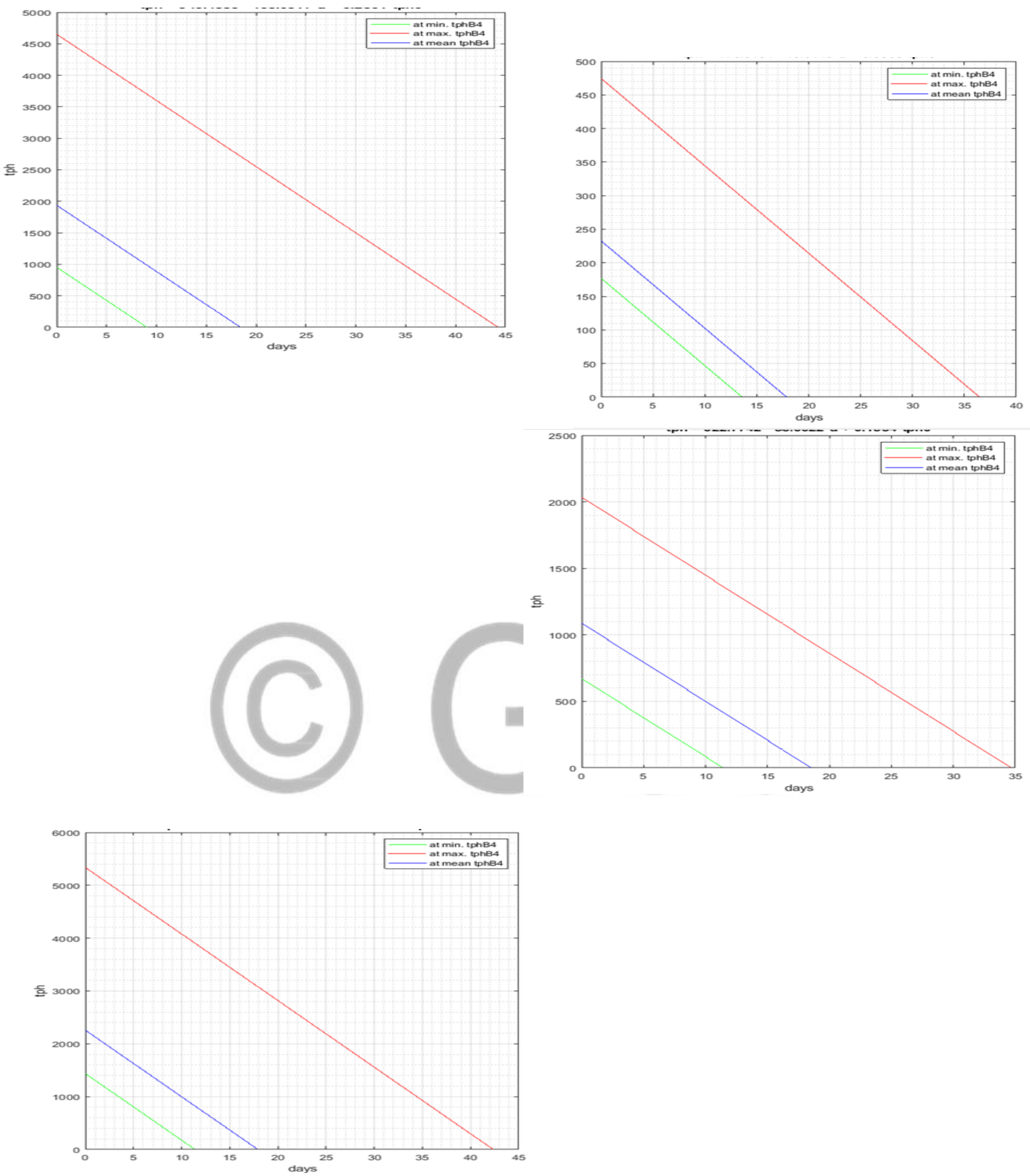


Figure 9(a-d): Rate of TPH Removal with respect to days using Multiple Regression Analysis

Conclusion and Recommendations

Hydrocarbon pollution management in engineered systems has proven viable, especially in environmental sustainability and biodiversity

The ANOVA model was developed to analyze data on soil contamination with treatment and incubation for 21 days using the one-way ANOVA. Extraction of data was done using Matlab codes with values of TPH in the treatment cells for all study areas. ANOVA was used to test change in TPH for control and treatments. With the independent variables ascertained, a mathematical link was determined using multiple linear regression (MLR) between the rate of TPH removal concerning days, and treatment, at each study area resulting in equations that can be used to determine the rate of TPH removal within a time frame.

The linear equation employed, (regression analysis) can be used as a tool to predict no of days for contaminant remediation for any polluted site within the same range of TPH values.

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