Experimental Analyses of the Physiochemical Parameters for Concentration Distribution in a Polluted Soil Medium

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Authors' contributions

This work was carried out in collaboration between authors DKK and OOA. Author DKK designed the study and wrote the introduction section. Author OOA managed the literature searches. Both authors performed the experimental analyses (methodology). Author DKK discussed the result of experimental analyses while author OOA wrote the conclusion section. At the end, both authors read and approved the final manuscript.

ABSTRACT

This experimental research was undertaken to show the concentration distribution of different physiochemical parameters in a soil polluted by crude oil. Various physiochemical parameters were investigated in the laboratory two months after extensive crude oil spillage using standard procedures. Five (5) soil samples were collected at different depths (0-0.1 m, 0.1-0.25 m, 0.25-0.4 m, 0.4-0.55 m and 0.55-1.0 m). The results of analyses revealed that the contamination of soil with crude oil caused PAHs, BTEX, TPH, nitrogen, and magnesium concentrations to decrease with increasing depth of the soil medium while soil PH, calcium and exchangeable acidity, hydrogen and

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aluminium concentrations to increase with increasing depth of the soil medium. Also, PH becomes more alkaline as crude oil contamination decreases. Predictive mathematical correlations were derived for each tested parameters from Microsoft excel charts to determine the extent of soil contamination. Therefore, the depth beyond which the soil is free from contamination can be determined from the equations correlated. This research shows different parameters that affects the growth of plants. Khana local government area (Ogoni) in Niger Delta, Nigeria is affected with the oil spillage, therefore, it implies low soil fertility, which in turns implies low agricultural productivity and reduced source of livelihood in the area. Hence, findings reveal the need for holistic and sustainable monitoring, control and remediation of the oil spilled environment.

1. INTRODUCTION

Since 1994, global production of crude oil condensate or natural gas has increased at an average of 1.5%. Extraction of oil either comes from onshore or offshore reservoir. 40% of global extracted oil comes from offshore. Onshore or offshore extractions are thereby susceptible to minor and major oil spill during extraction / production or transportation operation. This susceptibility was glaringly observed when oil rig exploded in the gulf of Mexico and released crude oil of about 60 000 barrel/day over a period of 3 months. Crude oil can be input into the soil through pipelines leakages, drilling sites, pumping stations, refinery, natural sources, ageing of pipeline, poaching of oil products and so on. From global perspective, more than eighty percent (80%) of crude oil spill near oil pipelines are due to poaching of oil products and so on [1,2].

Toxic hydrocarbons contained in crude oil can affect different species of wildlife and human in various ways. A particular concern is the ability of a fraction of crude oil to volatilize because it belongs to a class of toxicant known as Volatile Organic Compounds (VOCs). This is especially dangerous to oil spill clean-up workers who inhaled the harmful VOCs as they mitigate the spilled soil. Crude oil also contains Polycyclic Aromatic Hydrocarbons (PAHs) which are highly hazardous to human health since they are known carcinogens. They can induce malignant tumour that primarily affect the skin and other epithelial tissues [2]. PAHs are carcinogenic, mutagenic and teratogenic. Also, they are lipophilic since they are likely to be retained in the soil for many years and may even enter the aquatic environment inducing further hydrosphere pollution due to their hydrophobicity [3]. The accumulation of multiple sources PAHs in the soil may lead to the contamination of vegetables and food chains thereby posing a great health risk to humans.

The following remedial technology can be used; bio-venting, soil vapour extraction, solidification, solvent extraction, soil washing, photo extraction and so on. In recent years, method of biological remediation of oil contaminated soil is becoming more significant due to their ecological safety for the environment. Enzyme activities of the hydrocarbon-oxidizing micro-organism are used in the biological method for petroleum hydrocarbon degradation. According to De Jong [4], crude oil spillage on soil medium makes it unsatisfactory for plant growth. This is due to insufficient aeration of soil because of displacement of air from the spaces between the soil particles by crude oil [5].

The extent of migration of petroleum into the soil is greatly dependent on the volume of the petroleum discharged, the type of soil and other physical properties of the petroleum. If the volume is low, it will not affect the table water in any way although, it will migrate downward by action of gravity and capillary force until it becomes immiscible [6]. In previous studies, the more the volume of spilled petroleum, the deeper the oil migrates. Previous studies also enunciate that that the adverse effects of oil spill on vegetation includes the reduction in photosynthesis [7].

The incidence of oil pollution has been studied in many parts of the world [8]. Most importantly, various journal publications on spillage of oil containing similar information and new understanding on its effects on specific environmental components have been made [9]. In a study in Niger Delta Region of Nigeria, observed that hydrocarbons and heavy metals from crude oil negatively affected flora and fauna, enhanced the absorption and bioaccumulation of heavy metals in plant cells.

Oil pollution has been observed to cause death of hectares of mangrove forests and swamps as well it is impossible for plants to survive [10,11].

Contamination of soils by oil spills is a wide spread environmental problem that often requires cleaning up of the contaminated sites. Petroleum hydrocarbons adversely affects the germination and growth of plants by creating conditions which make essential nutrients like nitrogen and oxygen needed for plant growth unavailable to them [12].

Over six thousand (6000) spills had been recorded in the 40 years of oil exploration in Nigeria, with an average of one hundred and fifty (150) spills per annum. In the period 1976-1996, six hundred and forty-seven (647) incidents occurred resulting in the spillage of 2,369407 barrels of crude oil. Many authors have reported a lower rate of germination in petroleum or its derivatives contaminated soils [12,13,14,15]. The most common and important symptoms observed in the plants contaminated with oil and its by-products include the degradation of chlorophyll [16].

High concentration levels of hydrocarbon present in contaminated sites could pose a health risk to humans, plants and animal lives. In recent years, the release of hazardous and toxic substances into the soil, water sediments and air in Niger Delta, Nigeria has been a wide spread problems [9,17,18].

Studying the concentration distribution of crude oil in polluted soil by determining the physiochemical parameters goes a long way to determine the diffusion rate of the crude oil. Also, it will allow the researchers to determine the impact of oil on soil fertility and identify contaminants in the soil.

This research intends experimenting the results of different rate as a function of soil depth, properties of soil and quantity of oil spill. Method of mathematical correlation of results of the experimental data will be used. Experimental procedures showing different physiochemical parameters tested will be clearly shown.

2. MATERIALS AND METHODS

2.1 Materials

Polluted soil samples were collected after two months of extensive oil spillage from the Shell Petroleum Development Company (SPDC) site

at well 14, Yorla oil field, Khana Local Government, Rivers State, Nigeria. All standards were supplied by the Department of Petroleum Resources (DPR) and Federal Environmental Protection Agency (FEPA). Also, all QA/QC procedures relevant to sampling collections, custody and analysis were strictly adhered to according to American society of testing Materials (ASTM). The concentrated H_2SO_4, catalyst, K_2SO_4, NaOH and other reagents used were obtained from Chempro Limited, Port Harcourt, Nigeria. Analysis were carried out in the department of Chemical/Petrochemical Engineering and soil/crop science laboratories, both in the Rivers state university of science and technology, Nkpolu, Port Harcourt, Nigeria.

2.2 Equipment

Since different analyses were performed, the following equipment were used; Gas Chromatography, ASTM apparatus, conductivity meter, macro kjeldahl digestion, distillation apparatus, EPL flame photometer, PH meter, oven drier, photometer cells, magnetic stirrer for series of analysis performed. Also, glassware such as pipette, burette, and volumetric flasks were also used during the laboratory analyses.

2.3 Analyses

2.3.1 Total petroleum hydrocarbon (TPH)

In this analysis, the determination of TPH was performed on the samples by using a TRACE model 1300 Gas Chromatography (GC) equipped with helium as carrier gas. 10g of polluted soil samples were weighed in a 50 ml dual scale borosilicate glass beaker after which a reasonable amount of acidified Na_2SO_4 was added in other to remove the water content of the sample. This was followed by agitating the sample into a homogeneous powder form while adding CH_2Cl_2. The mixture was stored un-disturbed and then pass through cotton wool which serve as a filter material. Acetonitrite (CH_3CN) was then added to the filtrate to evaporate it to dryness. Finally, about 1L of di-chloro-methane (CH_2Cl_2) was used to rinse the bottle and the mixture carefully injected into the gas chromatography. The strip chart recorder of the gas chromatography measures and record the peak responses as produced by a plot of hydrocarbon content versus time. The amount is then summed up for the entire carbon- group detected to be of significance to obtain the total petroleum hydrocarbon.

2.3.2 Benzene, toluene, ethyl benzene and Xylene (BTEX)

Gas chromatography coupled to mass spectrometry (HP5890/HP5972) auto sampler HP7673 and software HPGB04C was used in this analysis. 200 g of soil sample was weighed and placed inside a containing vessel. 200 ml of water was measured using measuring cylinder and divided into four and shared into four different containers of 50ml each. The four containers were labelled accordingly; B, T, E, X. Mixture from each container were divided into five parts. The samples were all kept at room temperature with the aid of glass rod which was followed by drying at 106ºC for a period of 2 hours. The dried material was then disaggregated by crushing them into lumps. 20 ml of CH_3Cl was added into each sample and extraction was performed in a shake bottle for 2 hours. This was allowed to settle and the extract was transferred into a clean bottle using a flask funnel stuffed with cotton wool and Na_2SO_4 at the aperture of the funnel.

2.3.3 Polycyclic aromatic hydrocarbons (PAHs)

Polluted soil sample was collected into a soil container and refrigerated at 4ºC. This was later stored in amber bottle to minimize photolytic decomposition. A 60 ml methyl chloride (CH_3Cl) was added to the sample, sealed and shook for some minutes. The solvent obtained was transferred into a separate laboratory funnel and sample extracted by shaking the funnel for 2 minutes with periodic verification to release excess pressure. The CH_3Cl extract was collected and poured into a 250ml Erlenmeyer flask (CE-FLAS500 Pyrex, 500ml capacity). Second and third extractions were also carried out. The combined extract was then poured through a drying column containing about 10ml of anhydrous Na_2SO_4 and the subsequent extract collected in a Kuderna-Danish Concentrator (K-DC) (concentrator 89091-412 of 500ml flask and 100 ml tools). The Erlenmeyer flask and column were then rinsed with 25 ml of the CH_3Cl to complete the quantitative transfer. The Erlenmeyer flask was rinsed with 25 ml CH_3Cl to complete the quantitative transfer. The K-DC apparatus was placed in a hot water bath at a temperature (60-65ºC) so that the concentration tube is partially immersed in hot water. At required rate of distillation, the balls of the column will actively chatter. When the apparent liquid level reaches 1 ml, The K-D concentrator was removed and allowed to drain and cooled for 10 minutes. By refilling the sample bottle to 50 ml mark, and transferring the water to a 100 ml graduated cylinder, the original sample volume was determined and recorded.

2.3.3.1 Calculations

The concentration of PAHs could be calculated using the formular:

$$Concentration\ of\ PAHs\ \left(\frac{Mg}{L}\right) = (A\,V_t)/(V_i\,V_s)$$

A is the amount of material injected in monogram, V_t is the volume of total extract, V_i is the volume of extract injected in micolitre and V_s is the volume of water extracted in millilitre.

2.3.4 Nitrogen

Macro kjeldahl digestion with remote blower exhaust and distillation apparatus were used for the determination of nitrogen in the soil samples according to the method of Bremner [19]. The method was used because of its rapidness and simplicity. Reagents were carefully prepared (100 g K_2SO_4, 10 g $CUSO_4.5H_2O$) and NaOH dried and sieved. 8mg of soil sample was weighed using digitally sensitive weighing balance into a dry kjeldal flask. 20 ml of water was added and allowed to stand for 30 minutes. 11 g of the prepared K_2SO_4-plus catalyst solution was pipette and 30 ml of concentrated H_2SO_4 was measured using measuring cylinder in a fume cupboard for safety reasons. The flask was continuously heated until H_2SO_4 condenses about half way up to the neck of the flask. The flask was allowed to cool after which 100 ml of water was added forming a digest. The digest was transferred to a 1 litre Erlenmeyer flask. Sand residue in the flask was washed with 50ml of distilled water 4 times before the aliquot was transferred into Erlenmeyer flask. 50 ml of H_3BO_3 indicator solution was added and placed under the condenser for distillation. The kjeldahl flask was cleaned and the content of the flask was transferred into it. 150 ml of 10N NaOH was poured down the neck of the kjeldahl flask and was quickly attached to the distillation apparatus. The condenser was kept cool allowing sufficient water to flow through. About 150 ml of the distillate was collected and distillation ended. The ammonium ion in the distillate was titrated with standard sulphuric acid. Colour change from green to pink showed the end of titration

2.3.5 Potassium and calcium analysis

In these analyses, flame photometer with suitable filter for K and Ca were used. 5 g of soil sample was weighed and transferred into a 50 ml conical flask followed by the addition of 25 ml, 1M ammonium acetate (CH_3COONH_4). The mixture was shaken for 45 minutes and the extract was filtered into glass beakers. Aliquots of the filtrate were used to determine the potassium and calcium using flame photometer.

2.3.6 Magnesium

In the determination of magnesium, the Sherwood model 410 flame photometer that utilises low temperature flame was used. 1N solution of ammonium acetate ($C_2H_7NO_2$) was prepared and adjusted to pH of 7 using a PH10A model digital glass electrode pH meter. Magnesium standard solution was prepared which contains 1000 ppm Mg, 2000 ppm Ca, 125 ppm K and 50 ppm Na. Specific weight of polluted soil sample was measured into 50ml shaking bottle; 20 ml of the $C_2H_7NO_2$ was added. This was shaken for some minutes after which filtration using number 5 filter paper was used. Finally, a curve for the element was prepared by running series of standards using the flame photometer.

2.3.7 Soil PH

Soil PH was determined by the method of Bates [20]. A proportionate size of soil sample were measured and weighed into a 50 ml of distilled water. The mixture was agitated while at room temperature. This was followed by decanting the liquid with filter paper number 5 and its pH determined using a PH10A model PH meter

2.3.8 Total salt

20 g of soil sample was weighed into a 50ml shaking bottle. 20 ml distilled water was added and shake for 30 minutes. The solution was filtered using suction. The conductivity was determined using 26 solution-bridge which reads in Siemens per meter (S/m).

2.3.9 Exchangeable acidity, aluminium and hydrogen in polluted soil by titration

Exchangeable acidity was produced in polluted soil by the presence of exchangeable aluminium and hydrogen. The reagents used were potassium chloride (KCl), NaOH (0.01N) standard, 0.05N HCl standard, sodium fluoride (NaF) solution and phenolphthalein indicator. Apparatus used in the analysis were burette, centrifuge tubes with stopper, volumetric flask, 250 ml Erlenmeyer flask, and centrifuge and bottle shaker.

2.3.9.1 Procedures

5 g of air dried samples was made to pass through a 2mm sieve into 50 ml centrifuge tubes; 30 ml of 1N KCl was added. This was covered with stopper and shaken using reciprocal shaker. The content was centrifuged at 200 rotation for 15 minutes and later decanted into 100 ml volumetric flask. Another 30 ml of 1N KCl was added and shaken for 5 min. The content was again centrifuged and supernatant transferred into the same volumetric flask. This was done for the third time into the same volume of flask. The volume was marked up to 100 ml mark with 1N KCl. 50 ml of the KCl extract was pipetted into 250ml Erlenmeyer flask and 100 ml distilled water was added. 10 drops of indicator was added and the solution was filtrated with 0.01N NaOH to a permanent pink colour as end point with alternate sitting and standing. 1 drop of 0.05N HCl was added to the same solution in the flask to bring it back to the colourless condition after which 10 ml of sodium fluoride was added. While stirring the solution continuously, it was titrated with 0.05N HCl until the colour of the solution disappeared and does not return within 2 minutes.

3. RESULTS AND DISCUSSION

Different analyses were performed on crude oil polluted samples obtained from Niger Delta area of Rivers State, Nigeria. For better prediction of the concentration distribution of each experimented parameters, model equations derived from lines of best fit were shown. The correlated mathematical equations of each parameter were necessary to predict the depth when carrying out remediation process in the polluted soil medium. From the analyses of physiochemical properties of the hydrocarbon polluted soil, it was generally obvious that the extent of migration of spilled hydrocarbon is dependent on the volume discharge as shown in Table 1.

Table 1 depicts the results of experimented parameters of the polluted soil samples taken at various depths 0 to 1 m. Also, the equipment used for each analysis is shown.

Fig. 1 depicts the concentration of PAH along the depth of the porous soil medium after 2 months of extensive oil spillage. The concentration of

Polycyclic Aromatic Hydrocarbons (PAHs) increases with decreasing depth at the spill site with range from 0.45 to 0.1 mg/Kg. This trend reflects PAH enrichment in soil at a depth of 0.15 m which is the primary absorptive surface [21]. The PAHs enrichment is similar to results of previous study [22]. PAHs accumulate in the surface soil by adsorption because of their persistence and affinity for soil organic matter [23]. PAHs are known to constitute human health risk [24]. Hence, regular monitoring of spilled sites is highly recommended around residential quarters and source of drinking water. As shown on the chart, the equation that fits the curve is a polynomial of 2nd order. So, the equation represents the correlated mathematical model of the experimental values which can be used to determine the depth while carrying out remediation process for the contaminant (PAHs) in polluted soil medium.

Fig. 2 shows the concentration distribution of BTEX along the vertical depth of porous soil medium with a polynomial curve of 2nd order best fit the curve. Concentration of BTEX decreases with increasing depth of the soil. At about 0.8m depth of soil, there was no more crude left in the soil. So at a depth beyond 0.8 m, the soil was free from contamination, hence, during remediation, the depth should be dug above 1 m for proper remediation to take place. They belong to PAHs family and are also known to constitute human health risks [24].

Fig. 3 shows the concentration distribution of TPH along the vertical depth of soil. The logarithmic equation displaced on the chart will predict the concentration distribution along the soil depth. The concentration decreases with increasing depth of soil. This follows the same trend with the result of [25]. This shows that, at a very high discharge rate of petroleum, there will be greater effect of contaminant (TPH) on the soil. It can also migrate through the soil to the groundwater. Individual compounds of the TPH can separate from the original mixture, some will evaporate in the air while others dissolve into ground water and move away from the released area. Some other compounds might alter the particles in the soil and may stay in the soil for a long period of time.

Fig. 4 shows the nitrogen content of the soil as it decreases downward as the migration goes deeper into the soil medium. The result obtained is in agreement with the findings of [26] which say that in oil-polluted soils, nitrogen quickly become limiting to biodegradation of oil by micro-organism and plant growth. When the volume of spilled hydrocarbon is much, nitrogen will be in excess and can result in over-saturation of the growth of aquatic plants and algae. Excessive growth of these organisms in turn can affect water intakes which are harmful for plant growth. Also, the result shows that increase nitrogen soil content can affect the growth of the crops depending on the crop's nitrogen tolerance range. Excess of nitrogen will upset the balance between organic and inorganic nitrogen compounds ultimately leading to greater release of ammonium into the soil.
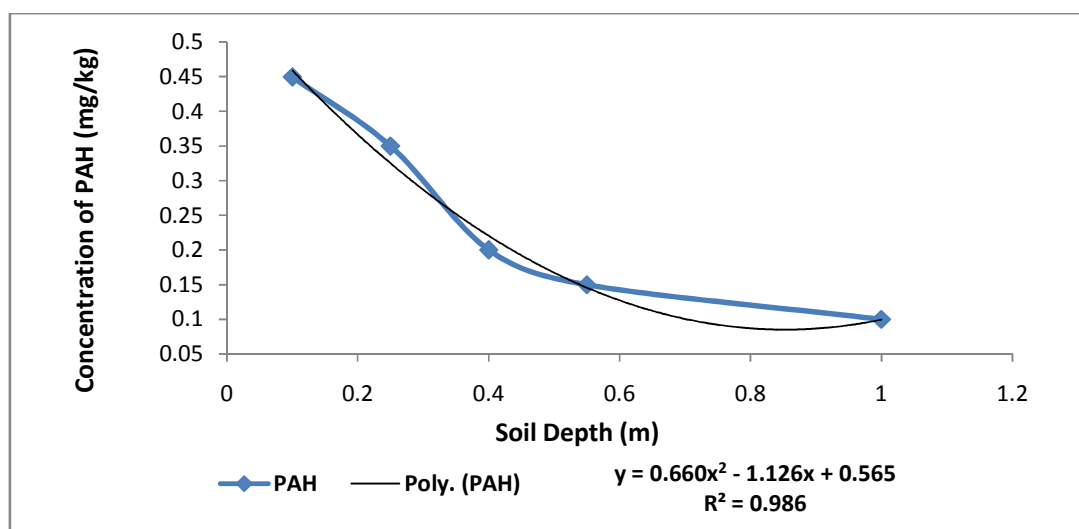

y = 0.660x^2 - 1.126x + 0.565
R^2 = 0.986

Fig. 1. Polycyclic Aromatic Hydrocarbon (PAH) content along the depth of the polluted soil medium

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Table 1. Result of physiochemical analyses of polluted soil samples

| S/N	Test parameters	Units	Soil depth					Equipment
			0.1m	0.25m	0.40m	0.55m	1.0m	
1	Polycyclic Aromatic Hydrocarbons (PAHs)	mg/kg	0.45	0.35	0.20	0.15	0.1	GC
2	Benzene, Toluene, Ethyl benzene, Xylene (BTEX)	mg/kg	0.05	0.04	0.03	0.02	0.01	ASTM
3	Total Petroleum Hydrocarbon (TPH)	mg/kg	1.2	1.1	1	1	0.9	K-D Apparatus
4	Nitrogen (N)	mg/kg	0.05	0.05	0.04	0.03	0.02	Kjeldahl digestion
5	Magnesium (Mg)	meq/100g	0.6	0.54	0.55	0.5	0.4	Flame photometer
6	Calcium (Ca)	meq/100g	2	2.5	3	3	3.8	Flame photometer
8	Soil PH		6.7	7.1	7.35	7.35	7.5	PH meter
9	Total salt	S/m	0.8	0.78	0.74	0.75	0.6	Centrifuge
10	Exchangeable acidity	mg/kg	0.48	0.58	0.68	0.78	0.8	Centrifuge
11	Exchangeable aluminum	mg/kg	0	0.02	0.04	0.06	0.08	Centrifuge
12	Potassium (K)	meq/100g	0.05	0.047	0.044	0.041	0.04	Flame photometer
13	Exchangeable hydrogen	mg/kg	0.48	0.56	0.58	0.64	0.72	Centrifuge
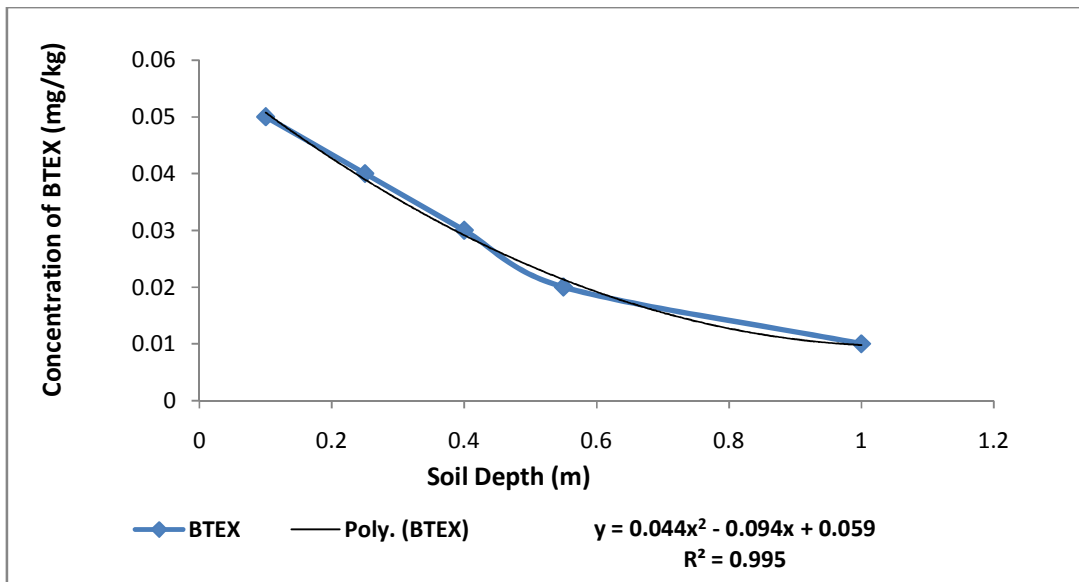
Fig. 2. Benzene, Toluene, Ethyl benzene and Xylene (BTEX) content along the depth of the polluted soil medium
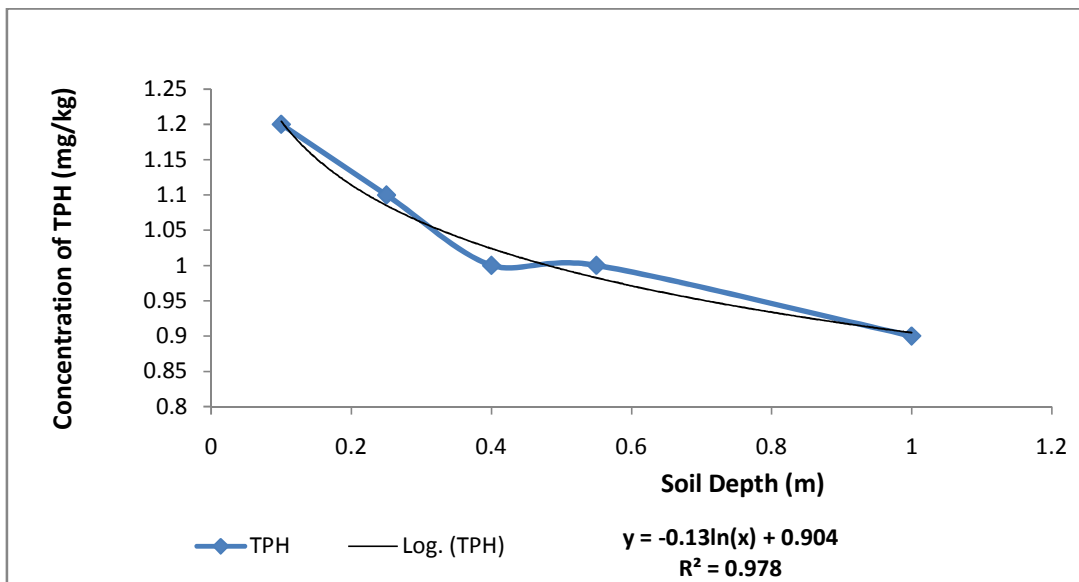

Fig. 3. Total Petroleum Hydrocarbon (TPH) content along the depth of the polluted soil medium

From Fig. 5, it can be deduced that magnesium content of the polluted soil medium also decreases exponentially along the vertical depth of the soil. The result obtained followed the findings of [27]. This shows that at high volume of hydrocarbon discharge rate, the extent of migration in the soil will be high thereby affecting lives of organisms necessary for plant growth. Magnesium deficiency will occur in seedling crops and pastures. Also, high level of magnesium in the soil can de-structure the soil which in turn makes the soil to lose its vital nutrients.

Fig. 6 displays the calcium content of the polluted soil; it increases along the depth of the soil. Also, it is expected that calcium content of polluted soil increases as pollution increases [27]. So, crude oil increases the calcium content of the soil. At a level lower than 0.5 meq/100 g,

there might be stubby, weakly branched and discoloured roots, fresh shoots dying at growing point. A calcium uptake by plants and microorganisms has a dual function in soil. It serves as an essential nutrient as well as the dominant base that keeps the soil natural in reaction. Depletion of calcium in the soil leads to the replacement of the calcium by hydrogen ions which make the soil to be acidic [28].

It can be seen from Fig. 7 that pH increases along the depth of the soil from 6.7 to 7.5. This is in agreement with the work of [28]. At a depth of 0.4 to 0.6 m, the pH remains constant at a value of 7.4 and thereafter increases in alkalinity. At low discharge rate of petroleum, it becomes very low at the sub-surface level making the soil to be slightly acidic which is dangerous for plant growth. Also, when discharge rate is high, the
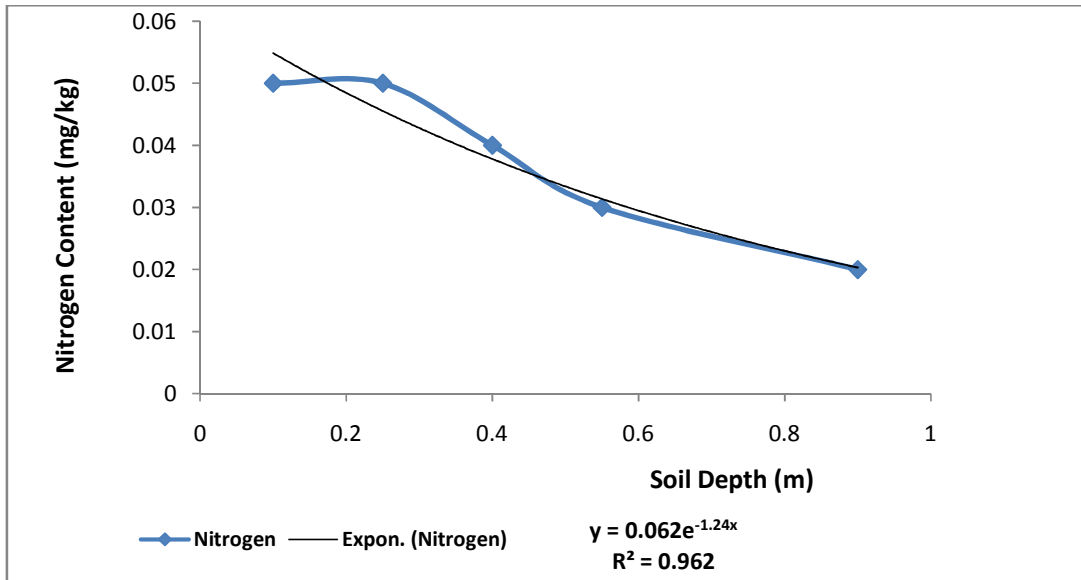

$$y = 0.062e^{-1.24x}$$
$$R^2 = 0.962$$

Fig. 4. Nitrogen content along the depth of the polluted soil medium

$$y = 0.620e^{-0.47x}$$
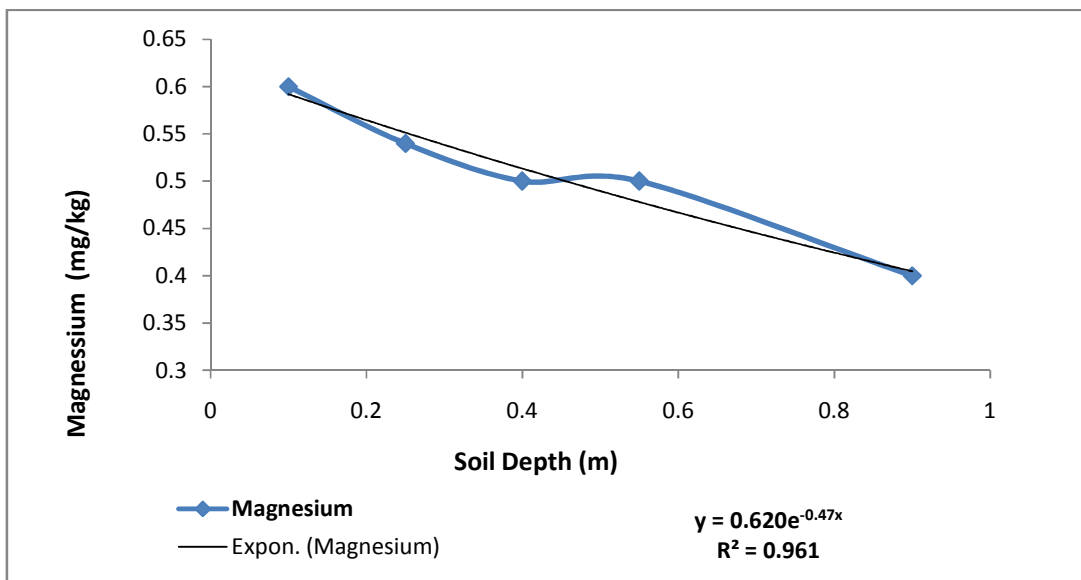$$R^2 = 0.961$$

Fig. 5. Magnesium content along the depth of the polluted soil medium

alkalinity of the soil increases leading to some plants nutrients becoming unavailable. The PH of soil influences the absorption of and the availability of nutrients to plants. There are two general sources of soil nutrients. Some nutrients are absorbed on colloids and some are available to plants as ions in solution [29]. Ideally, the average pH for plant growth is within 5 to 8. So, any pH values less or higher than the value specified can be detrimental to plant growth

which is very obvious in crude oil polluted soil environment.

Fig. 8 shows the content of exchangeable acidity along the vertical depth of the soil. The value increases from 0.45 at the surface to about 0.8 at a soil depth of 0.55 m. Generally, exchangeable acidity increase along the depth of the soil. This means that at high discharge rate of hydrocarbon, migration will be deep enough to reach and affect the water table, thereby
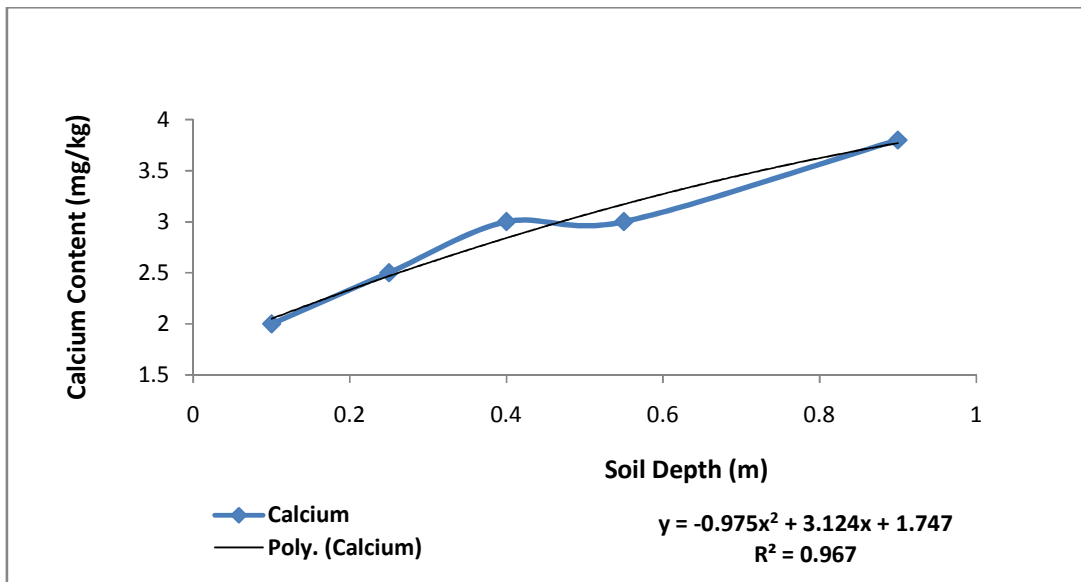

$$y = -0.975x^2 + 3.124x + 1.747$$
$$R^2 = 0.967$$

Fig. 6. Calcium content along the depth of the polluted soil medium

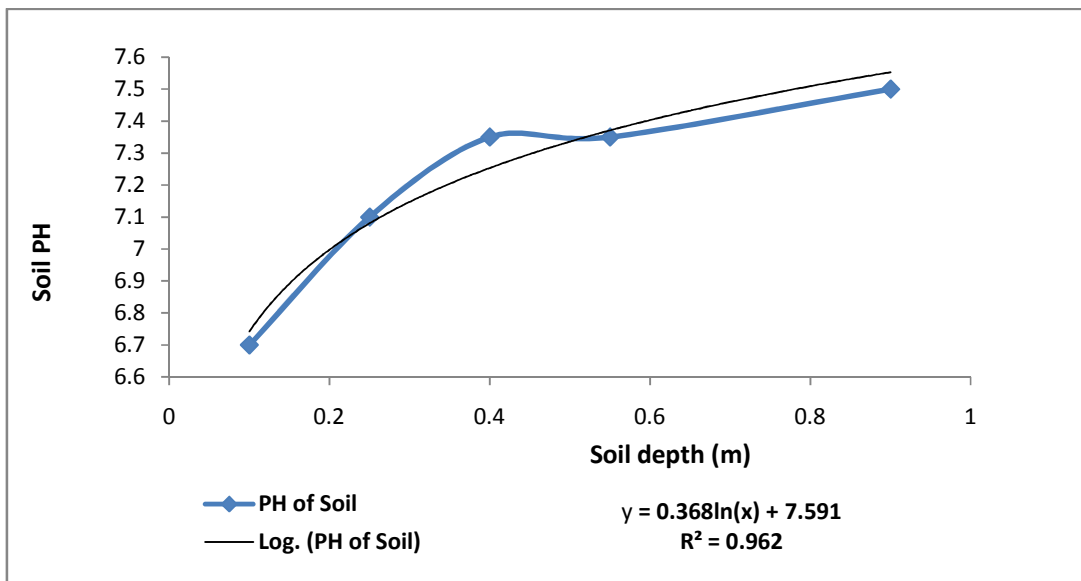

$$y = 0.368\ln(x) + 7.591$$
$$R^2 = 0.962$$

Fig. 7. Soil PH along the depth of the polluted soil medium

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affecting lives of human beings. This also explains in part, the toxicity of soils as a result of the release of aluminium and hydrogen ions into the soil by certain materials and this causes unfavourable soil condition for the growth of microorganisms, plants and animals [30].

Fig. 9 displays the total salt content of the polluted soil medium. The graph shows that the total salt content decreases down the depth of the soil. It shows the total concentration of all dissolved salt in the polluted soil medium. High salt level hinders water absorption inducing physiological drought in plants. As a result, plant roots will be unable to absorb adequate water due to unfavourable osmotic pressure. During germination and early growth, plants are most sensitive to salinity. This, without doubt can inhibit plant growth most especially when salinity leads to sodality (a secondary effect of salinity which has the ability to wash soluble salt into the soil). As salt increases, so also the electrical conductivity. Low conductivity values at different soil depths in the study area is an indication of high degree of leaching of nitrate salt taking place as a result of high rainfall in Niger delta [9]. Fig. 10 displayed content of potassium along the depth of the polluted soil. The content of potassium decreases from 0.05 to 0.038 along

the depth of the soil. This means that at a very high hydrocarbon discharge rate, plant growth will be inhibited. There will be stunted growth and reduced yield. The hydrocarbon content of the soil made the potassium content to decrease gradually thereby lacking important nutrients, reduces the stimulation of early growth, reduces protein production, reduces the efficiency of water and also reduces resistance to diseases.

Fig. 11 displayed content of exchangeable aluminium and hydrogen along the vertical depth of the polluted soil. This shows the ability of the polluted soil medium to hold and release various plant nutrients. Both physiochemical properties increase along the depth of the polluted soil. The increase is not favourable for plant growth since both aluminium (Al^{+++}) and hydrogen (H^+) are cation and at the same time acid formers. Neither are plant nutrients, so, since the content is increasing, it shows that at high hydrocarbon discharge rate, the soil will tend towards becoming an acid soil with a low pH. Exchangeable acidity is not simply due to hydrogen ions in the soil but is also due to the hydrolysis of aluminium derived from soil minerals. Exchangeable aluminium is one of the main factors that limits agricultural production in tropical climate regions [31].
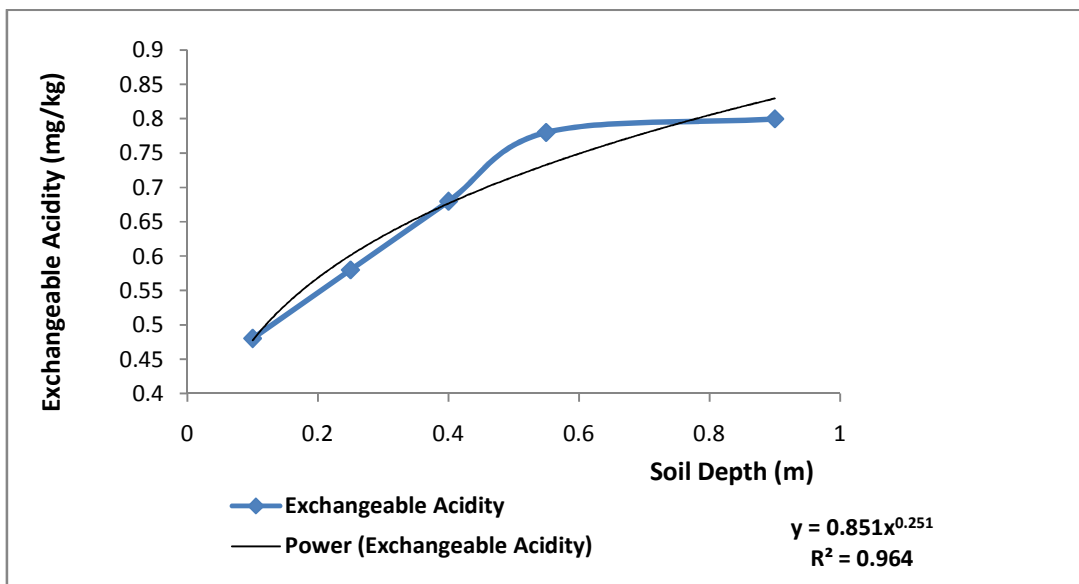

$$y = 0.851x^{0.251}$$
$$R^2 = 0.964$$

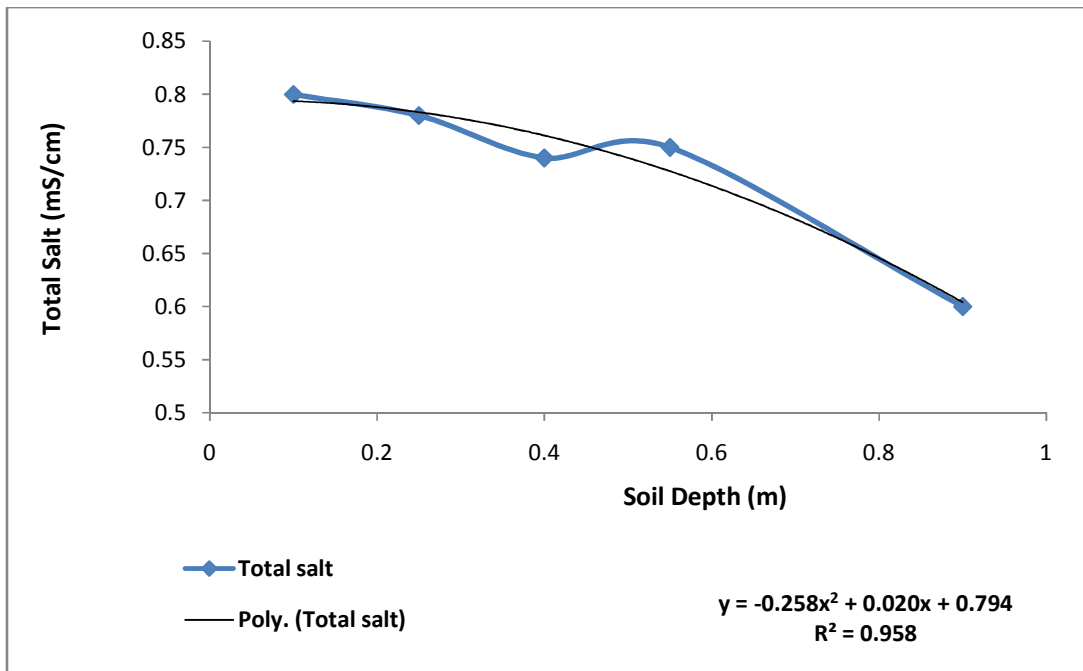**Fig. 8. Exchangeable acidity along the depth of the polluted soil medium**

Fig. 9. Conductivity (total salt) along the depth of the polluted soil medium
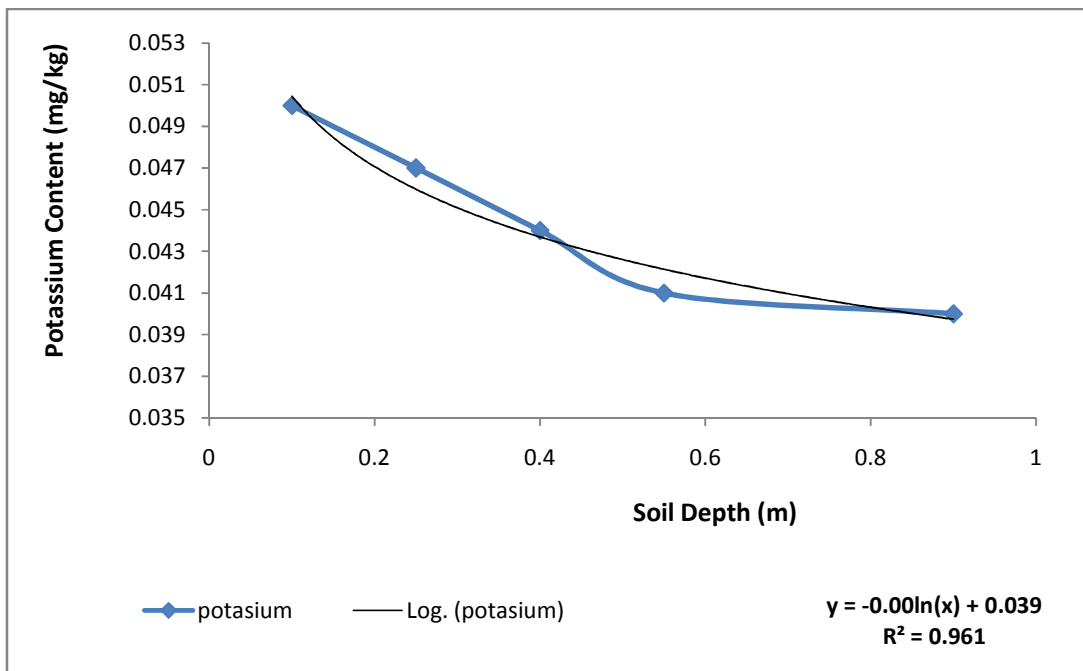

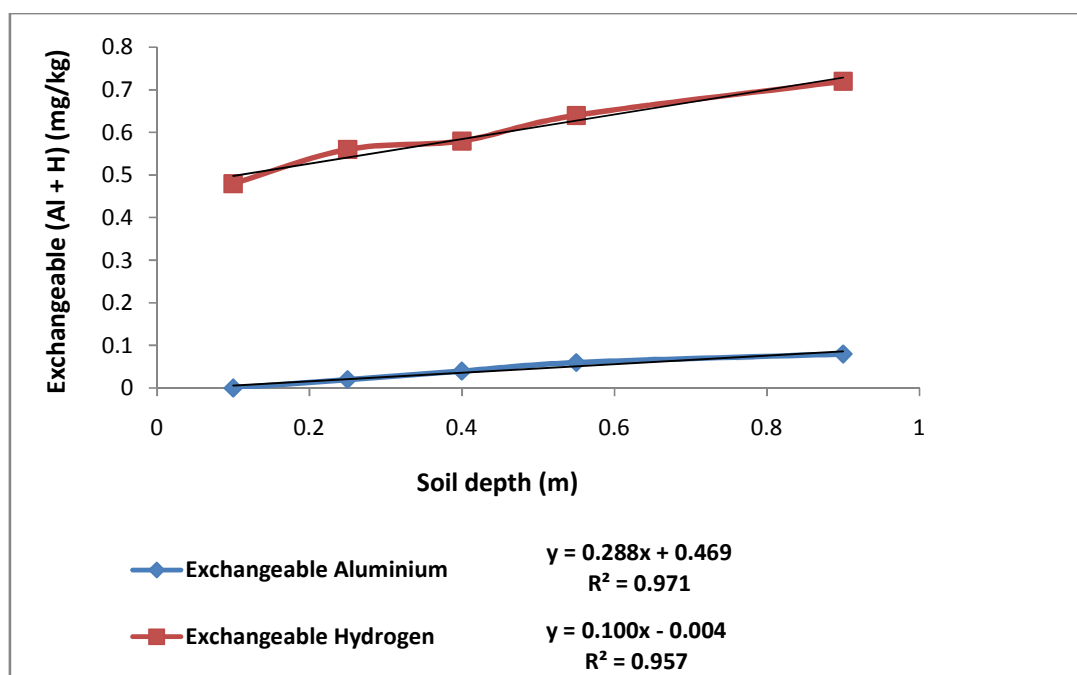**Fig. 10. Potassium content along the depth of the polluted soil medium**

Fig. 11. Exchangeable hydrogen and aluminium content along the depth of the polluted soil medium

4. CONCLUSION

This work has been able to examine by experimental analyses, the concentration distribution of important physiochemical parameters of a polluted soil medium. It was found out from the experimental analyses that the vertical diffusion rate of petroleum into soil depth is a function of quantity of oil spilled and also properties of the soil. Remediating a polluted environment for the benefit of the inhabitants becomes very crucial. The mathematical correlations (polynomial, exponential, linear and logarithmic) shown on the legends of each Figs. (1-11) predict the maximum depth of soil that will need to be dug during remediation of polluted soil. Therefore, the maximum depth at which a spilled petroleum will diffuse into the soil at migration time "*t*" can be predicted from the equations generated from the line of best fit.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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