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Total Petroleum Hydrocarbons Categories Concentration in Soils Within the Vicinity Housing Heavy-Duty Diesel Generators in Three Universities in Port Harcourt South-South Nigeria

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Abstract

Total petroleum hydrocarbons pollution of soil samples randomly collected from three Nigeria Universities in Port Harcourt due to the use of heavy-duty diesel generators was studied to ascertains the level of concentration of the different hydrocarbons' categories. The soil samples were collected at two different depths of 0.00-0.50m and 0.50-1.00m. The Universities were Ignatius Ajuru University of Education (IAUE), Rivers State University (RSU) and University of Port Harcourt (UNIPORT). The different total petroleum hydrocarbons categories were Gasoline Range Organics (GRO), Diesel Range Organics (DRO) and Lube Oil Range. Soxhlet extraction method was used in extracting the samples and due column clean-up was performed for chromatographic analysis. Gas Chromatography-Flame Ionization Detector was used to determine the level of concentrations of the different categories of total petroleum hydrocarbons. The results showed that at 0.00-0.50m depth, IAUE was 4.42145, 945.4784, and 525.66919 mg/Kg for GRO, DRO and lube oil range respectively, RSU was not detected, 494.44799 and 458.6715 mg/Kg for GRO, DRO and lube oil range respectively and UNIPORT was 4.40920, 501.2246 and 467.71426 mg/Kg for GRO, DRO and lube oil range respectively. At 0.50-1.00m depth IAUE was 2.75132, 596.35126, and 311.84451 mg/Kg for GRO, DRO and lube oil range respectively, RSU was not detected, 298.06899 and 270.61619 mg/Kg for GRO, DRO and lube oil range respectively and UNIPORT was 2.77780, 301.74701 and 276.88684 mg/Kg for GRO, DRO and lube oil range respectively. The level of soil contamination Showed that GRO > DRO > lube oil range. The observation showed that hydrocarbon pollution decreased with increase in depth. The level of DRO and lube oil range in the studied areas exceeded the limit acceptable and therefore adequate steps should be taken to remedy the situation so that it will not pose any health hazard to the workers operating the heavy-duty generators.

Key Words: Diesel, Heavy-Duty Generators, Gasoline Range Organics, Diesel Range Organics, Lube Oil Range, Pollution, Total Petroleum Hydrocarbons.

Introduction

In Nigeria, the inefficiency of the power sector to provide electricity all over the nation to serve the enormous power requirement needed has resulted in the installation of heavy-duty diesel generators in our industries, estates, universities, markets and even government houses. This condition has brought about the pollution of our environments especially petroleum hydrocarbons. The effects and challenges posed by this short fall in the supply of electricity through the National Grid as it is called in Nigeria has produced detrimental effects due to the contamination of the soil, water and air and the resultant health effect on human and plants is costly. At high concentration, petroleum hydrocarbons present in the soil produces health risk to animals, plants and even man [1]. The contamination and pollution of the soil, air and water by petroleum hydrocarbons has introduced hazardous wastes and substances that are toxic into the environments [2,3]. Crude oil easily contaminates the soil and several sources that produces the contamination includes fuel leakages from storage tanks, release of waste products, oil spills and deliberate discharge of petroleum products into the soil [4].

The discharge of total petroleum hydrocarbons and other pollutants associated with crude oil is alarming and the effect on the environment is of utmost concern to the world in general and therefore education of the public is necessary [5]. The effect of such pollution and contamination reduces the population and the dynamics of the ecosystem within the polluted site [6]. Advancement in technology has led to increase in the use of petroleum and its associate products, thereby increasing the level of toxicants in the environment which may be injurious, such as the impairment of body functions in animals [7]. Absorptions of these contaminants by microorganisms can lead to death and depopulation of non-resistant species, premature death and aging [8].

The use of heavy-duty engines to provide electricity in the campuses of the Nigerian Universities has solved a great deal of chemical energy requirements which would have been made void due to the lack of adequate power supply from the relevant authorities. This noted advantage also come with its attendant challenges of pollution due to spills associated with heavy duty generators [5]. Diesel is the main fractions or range of total petroleum hydrocarbons used in heavy duty engines and its non-volatile nature is detrimental to man and other organisms, both plants and animals [9]. Cell damage and asphyxiation also take place in plants and the soil available is grossly affected for agricultural use, since such land affected by diesel contamination can affect the growth of plants [10]. Environments contaminated by motor oil reduces its use by man and other organisms. This can result in the disruption of the ecological system and genomic integrity is also lost [11,12]. Due to the absence of laid down procedures for the disposal of sludge in tanks and the transfer of engine oils and diesel into these heavy-duty generators, there is the possibility of serious health threats when exposed to over a long period by workers [13].

A true knowledge of the amount of total petroleum hydrocarbons present in the soil of the heavy-duty generator sites in the universities can bring about effective prevention and decision-making process that can mitigate the release of petroleum products into the soil and hence effective remediation [14]. Adequate knowledge of the nature of petroleum hydrocarbons and the movement of the components in the soil will provide information that will be useful in understanding the nature of petroleum components movement in the soil and the toxicity level of such contaminants [15]. The presence of total petroleum hydrocarbons in the soil help in indicating the health status of the soil and may also be a useful tool in tracking the nature of contaminants in the soil although it is not a direct hazard pointer in the environment or man [16, 17]. This paper seeks to investigate the level of total petroleum hydrocarbons categories (groups and their percentage occurrence in the soils of three Nigerian universities located in Port Harcourt, Rivers State, where heavy-duty generators are mounted for the supply of electricity.

Materials and Method

Site Selection

Three sites were chosen for sampling from three universities in Port Harcourt Rivers State. The sample location points were from heavy-duty generator houses under the Estate and Works Departments of the Universities which uses diesel to power the electricity requirements of the various universities. The universities are Ignatius Ajuru University of Education (IAUE), Rivers State University (RSU) and the University if Port Harcourt (UNIPORT). The sites were chosen as a result of spillage of petroleum products on the soil during operation and repair works on the generators.

Soil Sample Collection

In order to reduce challenges during the sample collection, a survey was first carried out. Soil samples were collected at a depth of 0.0-0.5m and 0.5-1m within the study locations with the help of soil auger. 5-7 soil samples were taken at random in each location and then pooled together and mixed properly to form a composite sample. After each station sampling, the soil auger was thoroughly washed with clean water and allowed to dry at room temperature after being rinsed with methanol before taking samples from other sites. The collected samples were kept in previously washed containers that has been sterilized and then transported to the laboratory in an iced pack at 4oC.

Preservation, Extraction and Clean-Up of Soil Samples

Collected soil samples were preserved at 4oC in an ice chest and thereafter frozen at -10oC in a freezer to curb evaporation of volatile components of total petroleum hydrocarbons before sample extraction and clean-up is done. Soil samples were first homogenized by grinding with the aid of mortar and pestle for finer textures to be obtained. Pebbles, sticks stones and other solid particles were also removed during the process of obtaining finer particles. Soxhlet extraction method was used in this work according to U. S EPA method 3540 [18] and the method adopted by ASTM [19]. About 10g of the previously homogenized soil sample was weighed into a beaker and dichloromethane was added as a solvent of extraction, due to its ability and efficiency in not having interference with C5-C9, BTEXRWT. Extraction of soil sample was done within 14 days of sample collection. The clean-up of the chromatographic column was done by introducing a glass-wool into the column previously washed and dried to be free from other contaminants, then addition of silica gel into a beaker followed. Addition of dichloromethane was done by adding it to the beaker that already contains the prepared silica gel to become slurry in nature, and then anhydrous form of sodium sulphate was introduced into the chromatographic column. Addition of n-pentane was done after Sodium sulphate has been added into the chromatographic column. A mixture of the concentrated sample with cyclohexane was put into a beaker and then added into the prepared column. n-Pentane was used in order to elute the samples and then collected at the bottom of the chromatographic column. The addition of more pentane was required to the system for more elution of the sample to be obtained in the process. The eluted soil samples were then evaporated to dryness after the column has been rinsed with dichloromethane. The method used by were adopted in soil samples clean-up procedures [20, 21].

Soil Samples: Separation and Detection

The use of Agilent 6890N Gas Chromatography-Flame Ionization Detector (GC-FID) was employed in the detection of total petroleum hydrocarbons concentrations in soils of the locations under study (Cortes, 2012). A 3µl concentration of the clean-up sample was injected with the help of a micro-syringe through the vial of the GC. The syringe was previously cleansed by the use of blank dichloromethane injected into the micro-syringe. The micro-sy-

ringe was cleansed thrice with dichloromethane before it was then for the analysis of the sample. After the sample has been rinsed with the previously eluted sample, then the soil sample was again introduced with the aid of the syringe into the chromatographic column for the different hydrocarbons components to be separated during the process of the analysis. The different components of total petroleum hydrocarbons within the separated sample was then detected by the Flame Ionization Detector. The resolution of the different total hydrocarbon components was then achieved at a certain chromatogram, and then measured in mg/Kg for that particular soil sample is the quantity present.

Results and Discussion

The results of total petroleum hydrocarbons analysis for the different categories at the depths of 0.00-0.5m and 0.5-1.0m are illustrated in Tables 1 and 2. In Table 1 (0.00-0.5m), Gasoline range organics (GRO) were IAUE, 4.42145mg/Kg; RSU, not detected and UNIPORT, 4.40920mg/Kg; Diesel range organics (DRO), were IAUE, 946.4584mg/Kg; RSU, 494.44799mg/Kg and UNIPORT, 501.2246mg/Kg and lube oil range were IAUE, 525.66919mg/Kg; RSU, 458.6715mg/Kg and UNIPORT, 467.71426mg/Kg. In Table 2 (0.5-1.0m), Gasoline range organics (GRO) were IAUE, 2.75132mg/Kg; RSU, not detected and UNIPORT, 2.77780mg/Kg; Diesel range organics (DRO), were IAUE, 596.35126mg/Kg; RSU, 298.06899mg/Kg and UNIPORT, 301.7470mg/Kg and lube oil range were IAUE, 311.84451mg/Kg; RSU, 20.61619mg/Kg and UNIPORT, 276.88684mg/Kg. The results from Tables 1 and 2 indicated that the concentrations of the hydrocarbons categories were in the order IAUE > UNIPORT > RSU, for all the ranges of hydrocarbons studied. A clear observation from the results indicated total petroleum hydrocarbons concentrations in the soils decreased with increase in depth, which agreed with [1], whose report revealed that total petroleum hydrocarbons decreased as the depth moved from top soil to subsoil from soil samples in Ikot Ada, Akwa Ibom State. The results also agreed with the findings of during a study on the level of total petroleum hydrocarbons in soil of an oil polluted area in the Niger Delta [22].

Petroleum hydrocarbons which includes lubricating oils, gasoline and diesel oil find their way into the soil in this case as a result of spill due to transfer of diesel to the generators, servicing work on the engines and leakages from the generator parts and therefore diffuse and pollute the soil. This scenario is similar to that observed by [23]. This affect the soil organisms within the area making them to change location due to changes in the soil composition and the entire environment [24]. High concentration of total petroleum hydrocarbons in the soil creates unfavorable conditions in the soils by reducing diffusion of gases and increase of anaerobic organisms which helps in decreasing available oxygen due to the anoxic conditions created by the oil films on the surface and sub-surface of the soils involved [25]. Exposure to hydrocarbons at elevated levels by workers may result in dermatitis, when the skin is in regular contact with petroleum hydrocarbons. Other effects associated with hydrocarbons contact include myelin loss, causing disorder in the central nervous system, kidney and blood diseases [26, 27]. During rain there is the possibility of drift (since most heavy-duty generators are always at elevated positions) to the surrounding farmlands and thereby making the farmlands not too useful for agricultural purposes due to the hydrocarbons' contamination [28]. It is significant to note that GRO contains more straight-chain hydrocarbons as compared to DRO, hence the toxicity effect to workers will be minimized since more components are known to be present in gasoline than diesel and lube oil [15]. Which are the primary fuels used in heavy-duty diesel generators and gasoline may only be used during maintenance.

Table 1: Total Petroleum Hydrocarbons Groups Concentrations in the Soils of the Universities Heavy-Duty Generator Sites at 0.0-0.5m depth

Stations	Total Petroleum Hydrocarbons Groups		
	Gasoline Range Organic (GRO) C_6-C_{10}	Diesel Range Organic (DRO) C_{11}-C_{28}	Lube Oil Range C_{29}-C_{40}
IAUE	4.42145	945.4784	525.66919
RSU	-	494.44799	458.6715
UNIPORT	4.40920	501.2246	467.71426

Table 2: Total Petroleum Hydrocarbons Groups Concentrations in the Soils of the Universities Heavy-Duty Generator Sites at 0.5-1.0m depth

Stations	Total Petroleum Hydrocarbons Groups		
	Gasoline Range Organic (GRO) C_6-C_{10}	Diesel Range Organic (DRO) C_{11}-C_{28}	Lube Oil Range C29-C40
IAUE	2.75132	596.35126	311.84451
RSU	-	298.06899	270.61619
UNIPORT	2.77780	301.74701	276.88684

The percentage composition of the concentration of total petroleum hydrocarbons for the different categories at the depths of 0.00-0.5m and 0.5-1.0m are shown in Tables 3 and 4. In Table 2 (00-0.5m), Gasoline range organics (GRO) were IAUE, 0.003%; RSU, 0.00% and UNIPORT, 0.005%; Diesel range organics (DRO), were IAUE, 64.08%; RSU, 51.88% and UNIPORT, 51.73% and lube oil range were IAUE, 35.917%; RSU, 48.12% and UNIPORT, 48.265%. In Table 4 (0.5-1.0m), Gasoline range organics (GRO) were IAUE, 0.003%; RSU, 0.00% and UNIPORT, 0.005%; Diesel range organics (DRO), were IAUE, 65.46%; RSU, 52.41% and UNIPORT, 51.90% and lube oil range were IAUE, 34.53%; RSU, 47.59% and UNIPORT, 48.095%. The results from Tables 3 and 4 indicated that the percentages of the various ranges remained almost the same within the two different depths, which means that the rate at which the different categories percolated through the soil strata were the same. Although, total petroleum hydrocarbons decreased in the soil as the soil depth increased, and the percentages of the various hydrocarbons' groups remained the same the hydrocarbon quantity have greatly reduced. The low presence of the hydrocarbon ranges at greater depth probably due to the low permeability of soil this is advantageous to man since the low permeability will result in low migration to the groundwater and hence low risk of contamination of the groundwater [29, 30]. The high presence of diesel range organics followed by lube oil range is shown in the level of percentage presence in the soils. This may be due to the low volatility of diesel and other higher fractions of total petroleum hydrocarbons and the residual accumulation of these fractions gave rise to the high level of concentration. The total or near absence of the gasoline range organics may be due its non-usage in diesel engines and the little quantity observed in IAUE and UNIPORT might have possibly arisen due to repair works on the generators during the time of study, for petrol is often used in washing engine parts to remove grease and dirt due to its ability to dissolve substances. The high rate of volatility of the gasoline group might have also caused the low availability of the range.

Table 3: Total Petroleum Hydrocarbons Categories Percentage Concentrations in the Soils of the Universities Heavy-Duty Generator Sites at 0.0-0.5m depth

Stations	Total Petroleum Hydrocarbons Groups,		
	Gasoline Range Organic (GRO) C_6-C_{10}	Diesel Range Organic (DRO) C_{11}-C_{28}	Lube Oil Range C29-C40
IAUE	0.003	64.08	35.917
RSU	0.00	51.88	48.12
UNIPORT	0.005	51.73	48.265

Table 4: Total Petroleum Hydrocarbons Categories Percentage Concentrations in the Soils of the Universities Heavy-Duty Generator Sites at 0.5-1.0m depth

Stations	Total Petroleum Hydrocarbons Groups		
	Gasoline Range Organic (GRO) C_6-C_{10}	Diesel Range Organic (DRO) C_{11}-C_{28}	Lube Oil Range C_{29}-C_{40}
IAUE	0.003	64.08	35.917
RSU	0.00	51.88	48.12
UNIPORT	0.005	51.73	48.265

Petroleum products are found in large concentrations in the soils of the studied areas and the toxicity/health effects of the total petroleum hydrocarbons groups as characterized by [31] are shown in Table 5. The total petroleum hydrocarbons fractions are not assessed for cancer potency but only provided the toxicological status of some components [32], as seen in Table 5. Petroleum hydrocarbons naturally is composed of several chemical compounds which produces several challenges in humans, such as diseases in workers assigned to the heavy-duty generators threat to soil organism525.s, neurological disorders, pulmonary disease, which may be noticed in a short-term or long-term [33]. Exposure to certain components found in total petroleum hydrocarbons like benzene, toluene and xylene have significant effect on the liver, kidney and blood of the workers [34]. Gasoline leakage into the soil have the ability to stick to the soil particles thus may be exposed to human, contact and also move downwards to affect the groundwater of such environment [35]. Workers are at target risk due to contact and inhalation of total petroleum hydrocarbons exposure, for there are health risks when exposed to total petroleum hydrocarbons contaminations through dermal contact, ingestion and inhalation [5]. The total absence of rules guiding the disposal of petroleum hydrocarbons from tanks, how diesel and engine oils are transferred into the heavy-duty generators provides a means through which workers will have contact with petroleum hydrocarbons and such poses significant threat to life when exposed to over a long period, since most components of total petroleum hydrocarbons are recalcitrant and chronic with life-threatening and endangering after effect [36, 13].

Table 5: Total Petroleum Hydrocarbons Components Cancer and Minimal Risk Levels Classifications

TPH (Component)	EPA Cancer Classification	MRL (Oral)	MRL Inhalation (ppm)
Gasoline	na	na	na
Diesel	Group D	na	0.02mg/m^3
Engine oils	na	na	na
Jet fuels	Group A	na	9mg/m^3(IN, JP-4 fuel)

EPA Classification for cancer, A – carcinogenic to human, B2 – probably carcinogenic to human, C – possibly carcinogenic to man, D - not classified as being carcinogenic to human, na – no available data
Period of exposure: AC – acute (≥ 14 days), IN – intermediate (15 to 365 days) and CR – chronic (≥ 365 days)

Conclusion

This work revealed that different soil samples analyzed from the three universities sites housing heavy-duty diesel generators were contaminated with total petroleum hydrocarbons. The results indicated that the levels total petroleum hydrocarbons in the soils have reached unacceptable limits as proposed by DPR and therefore may pose serious health hazard to workers and operators of the heavy-duty generators employed by the universities, due to regular contact with the hydrocarbon products in the soils and the engines. The various universities should not drill bore holes near these generator sites, since there is the possibility of total petroleum hydrocarbons leaching through the soil to the groundwater within the immediate surroundings of the heavy-duty generator sites. Remediation processes should be put in place by the various universities' authorities so that the presence of total petroleum hydrocarbons will be at an acceptable minimum within the environments of the heavy-duty generator sites.

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