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Levels of Total Petroleum Hydrocarbons in Asphalt contaminated soil from selected areas of Port Harcourt

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Abstract The levels of Total Petroleum Hydrocarbon (TPH) using Gas Chromatography Flame Ionization detector (GC/FID) in asphalt contaminated soils from three Asphalt Companies of AUC, H & H and JAFAC in Port Harcourt environment were examined. The total concentrations and standard deviation of TPH across the three studied areas showed that AUC Asphalt had 2037±423.7 mg/Kg, H & H Asphalt had 1934±664.5 mg/Kg and JAFAC Asphalt had 1501±479.7 mg/Kg. The mean concentration was 1824±522.6 mg/Kg. The result showed that AUC Asphalt soil area was more contaminated than the other two areas. These concentrations were above the permissible limit as given by DPR. The effect of TPH will be detrimental to the health of individuals in these areas that carry out farming activities in the farm land where soil samples were collected. It is therefore necessary for actions to be taken for the remediation of the area.

Keywords Total Petroleum Hydrocarbon, Asphalt, Soil Contamination and Port Harcourt

Introduction

Metropolitan top soil has remained extremely altered, affected and changed through the activities of man. The close up of soil is essential for transport and infrastructural growth. The process of closing up or surfacing of soil in most cases is associated with negative effects on the normal functions of the soil in the ecosystem. Nevertheless, closed or surfaced soils can perform critical roles in the cycling of materials by ground surfaces in metropolitan environments. An urban area is well-defined by the rigorous and extensive anthropogenic influences, which repeatedly give negative influence and creates a contiguous atmosphere or situation [1]. The metropolitan city of Port Harcourt and its environs have exceptionally established ecological system produced by its large human population, which is a modification from the original ecosystems that earlier existed prior to human interference [2].

In city settlements, soil surfaces are frequently and rigorously transformed by the activities of man and these modifications render the affected soil differ from those in other areas that have not be interfered with, which at the initial were in the same condition. Academics have categorized soils within urban settlements as soils that have been modified to gigantic organisations and structures which had been rendered not suitable for agricultural purpose because of little nutrients that can be obtained, elevated pH levels, little organic matter content and pollution by heavy metals, salt and other chemical impurities.

Petroleum is a complex mixture of hydrocarbons (aliphatic and aromatic) and organometallic complexes such as heavy metals (vanadium, chromium, nickel etc.). Petroleum differs extensively in structure and physical characteristics. There are many chemicals that are gotten from degradation, combustion and reactions involving petroleum and its allied chemicals. From petroleum other substances such as polycyclic aromatic hydrocarbons, benzene, xylene, phenol and other emergent organic contaminants are formed. Petroleum hydrocarbon is commonly

used to refer to compounds which contain only hydrogen and carbon, whose origin is from the crude oil. The term total petroleum hydrocarbons (TPH) is used to refer to the quantity of petroleum-based hydrocarbons found in an environmental matrix that can be measured.

Accordingly, while petroleum hydrocarbon deals with a complete and slightly insubstantial amount, TPH is concerned with the definite results obtained through sampling and analysis. There are three main groups of chemical compounds present in crude oil, which are the alkanes (paraffin), alkenes (olefins) and aromatics. According to a report [3], there was a high concentration of TPH in dust collected from petrol stations, roads at high traffic congestion points and domestic areas in Tshwane urban area in South Africa. They observed higher TPH value in petrol stations than the other areas examined. Elevated levels of hydrocarbons in an environment constitute pollution and as such puts humans, plants and animal living within the area at risk of different health issues. Presently, the discharge of harmful and deadly constituents into the soil, water, sediment and air in Niger Delta, Nigeria has taken a new and larger dimension [4-7]. Contaminants in the environment are widely distributed because of increased number of services and developments and are affecting human well-being, aquatic resources, ecologies and other receiving bodies.

The release of industrial effluents containing high concentrations of toxicants has the capacity to affect the receiving body. Some of the major factors that lead to environmental pollution are either natural or anthropogenic activities, which include pesticides application [8], food processing [9], oil and gas exploration and sand dredging [7].

The aim of this study therefore, determines the concentrations of total petroleum hydrocarbons in mixed asphalt contaminated soils from three asphalt plants areas within Port Harcourt, Rivers State of Nigeria.

Materials and Methods

Sample Collection

Soil samples were collected with soil auger at a depth of 0-20cm at the mixed asphalt plant soil of the two other samples 3 meters away east and west of the first sampling point. These samples were aggregated as composite sample for each of the asphalt sites. The samples were well packaged and labelled accordingly.

Determination of Total Petroleum Hydrocarbons

Soil Sample Extraction

Ten (10g) grams of soil sample was put into a yellow coloured glass bottle and mixed with a water free sodium sulphate (Na_2SO_4) in the bottle. The sample/sodium sulphate mixture was stirred to homogeneity. The work of the Na_2SO_4 is to remove water that might remain in the soil sample. A known volume of 300 µg/ml of 1-chlorooctadecane standard was also mixed with the soil/ Na_2SO_4 mixture. An addition of 30 ml dichloromethane (DCM) was put into the mixture to effect extraction of TPH in the soil sample and was tightly closed. All the content was transferred to a mechanical stirrer. The sample was shaken for a period of 5 to 6 h using mechanical stirrer and allowed to settle for 1 hr. Thereafter, the content was filtered with 110mm filter paper into a beaker. The filtrate was concentrated to 1 ml by allowing it to evaporate freely for twelve hours in fume cupboard.

Sample Analysis

Identification of the total petroleum hydrocarbon content of the soil was achieved by using agilent 6890N gas chromatography – flame ionization detector (GC-FID) apparatus [10]. Precisely, 3µl of the concentrated sample was used to clean the syringe which was finally used in transferring the sample to the chromatographic instrument. The FID identifies the compounds present in the sample and the concentration of TPH determined at a specific chromatogram in mg/Kg.

Results and Discussion

Total Petroleum Hydrocarbon Content of the Soil Samples

The result of the total petroleum hydrocarbon in the soil samples from the three asphalt plant studied is given in Table 1, while figure 1 showed the total TPH and the mean value.

Table 1: The concentration (mean±std) in mg/kg of total petroleum hydrocarbon in soil samples from the asphalt study area

Components	AUC Asphalt	H & H Asphalt	JAFAC Asphalt	Control
C8	1.325±0.956	48.53±8.076	ND	ND
C9	23.24±4.765	8.579±4.987	ND	ND
C10	74..97±10.46	188.1±66.09	23.47±7.894	0.015±0.002
C11	33.63±11.74	131.1±45.78	ND	ND
C12	187.0±22.23	170.3±58.90	24.37±5.875	0.012±0.003
C13	110.9±16.81	191.9±64.01	24.78±10.86	ND
C14	76.39±19.08	155.9±43.22	22.58±2.784	ND
C15	55.82±7.642	34.45±12.33	120.2±30.67	ND
C16	90.91±30.17	160.9±55.40	121.3±56.90	0.242±0.054
C17	239.5±42.90	144.5±41.93	132.4±70.06	2.412±0.746
Pr	175.0±18.95	142.4±71.00	119.3±43.12	ND
C18	140.9±24.52	23.24±8.996	134.9±24.44	1.023±0.233
Ph	119.8±5.689	110.8±27.88	ND	ND
C19	133.9±34.86	114.2±12.12	24.33±4.890	1.032±0.423
C20	127.0±41.23	2.062±0.065	123.0±53.84	1.123±0.094
C21	165.6±32.11	143.3±87.26	119.3±32.11	ND
C22	134.0±14.13	25.53±14.13	12.99±3.098	ND
C23	121.2±78.52	116.1±38.13	14.92±6.987	ND
C24	12.13±2.543	9.932±1.907	15.41±5.099	ND
C25	8.132±2.888	7.405±2.024	120.9±59.08	1.043±0.843
C26	5.139±1.489	4.992±0.234	19.38±4.074	ND
C27	ND	ND	22.86±6.973	ND
C28	ND	ND	123.2±20.03	ND
C29	ND	ND	27.23±4.876	ND
C30	ND	ND	25.82±12.05	ND
C31	ND	ND	128.1±14.01	ND
C32	ND	ND	ND	ND
C33	ND	ND	ND	ND
C34	ND	ND	ND	ND
C35	ND	ND	ND	ND
C36	ND	ND	ND	ND
C37	ND	ND	ND	ND
C38	ND	ND	ND	ND
C39	ND	ND	ND	ND

ND=NOT DETECTED Pr = Pristane, Ph = Phytane

The concentrations of the individual compounds or fractions of total petroleum hydrocarbons in soil samples from the study area are shown in Table 1. Individual concentrations of TPHs ranged from non-detectable limit to 239.5±42.90mg/Kg. The AUC asphalt study area had range of ND to 239.5±42.90mg/Kg, with the highest concentrations recorded for C-17 (239.5±42.90mg/Kg), pristane (175.0±18.95 mg/Kg), C-21(165.6±32.11mg/Kg) and C-12(187.0±22.23mg/Kg) respectively. For H & H asphalt area, the range was from ND to 191.9±64.07 mg/Kg, with highest concentrations for C-13(191.9±64.07mg/Kg), C-10 (188.1±66.09 mg/Kg), C-12 (170.3±58.90 mg/Kg) and C-16 (160.9±55.40 mg/Kg). JAFAC asphalt ranged from ND to 164.9±24.44 mg/Kg and the highest concentrations were found in C-18 (164.9±24.44 mg/Kg), C-17 (132.4±70.06 mg/Kg), C-31 (128.1±14.01 mg/Kg), C-20 (123.0±53.84 mg/Kg) and C-25 (120.9±59.08 mg/Kg) respectively.

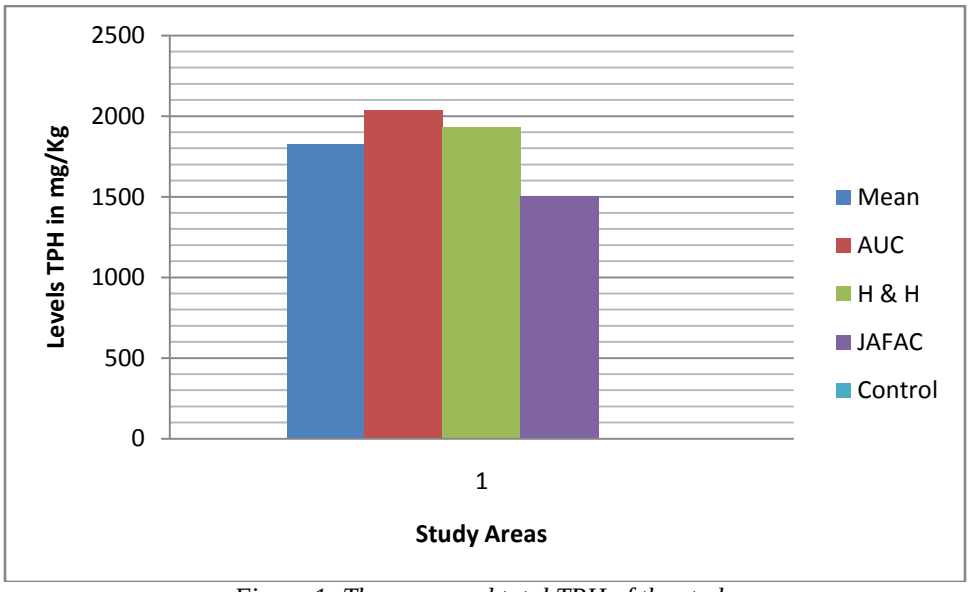

Figure 1: The mean and total TPH of the study

The total petroleum hydrocarbons for each of the area were AUC asphalt (2037±423.7 mg/Kg), H & H asphalt (1934±664.5 mg/Kg) and JAFAC asphalt (1501±479.7 mg/Kg). The value observed for the control sample was 6.902±2.398 mg/Kg, which was lower than the value of the experimental stations. A comparative evaluation of the concentrations of the individual fractions or constituent of TPH in the asphalt production sites with those of control revealed that TPH were more concentrated at the asphalt mix sites than the control areas. According to Hanson *et al.*, [11], the different ranges of TPH classification are C4 – C9 carbon chain length, classified as gasoline and condensate range organics (GRO), C10 – C24 carbon chain length, known as diesel range organics (DRO) and > C28-C35 chain length referred to Lube oil range. The results from the individual stations showed that in AUC, the major TPH contaminant in the soil were the hydrocarbons that fall within the range and category of diesel range organics. This was so because the study area mostly use diesel to power their plants and most cases spills of diesel occur. The entirety of the area examined within the AUC vicinity are subject to partial flooding at the instance of heavy rain, which distributes the diesel contaminants around the Asphalt plant area, thereby causing a distribution effect of the diesel range organics within this site. The lower fractions (gasoline and condensate range organics) were generally lower in concentration in the examined stations when compared to the diesel range organics. This is due to the physical property of volatility these fractions of hydrocarbons possess, which is very pronounced in very hot periods or seasons of the year. Another factor that affects their volatile nature is wind and wave (in case of river). the lighter fraction aromatic hydrocarbons evaporate rapidly. For H & H, the results obtained indicated the same as the previous one, which was between n-C8 to n-C25, and the Diesel Range Organic (DRO) were dominant. The abundance of low molecular weight hydrocarbons (<n-C23) suggested that the contamination of this sample may have been recent. JAFAC asphalt had a slight variation from the other two areas as it DRO was dominant but with a little lube bay oil which may from heavy duty and generator repair processes.

This work was far above reports by Adeniyi and Afolabi [12] at 399.83, 362.60 and 356.20 µg/g and Hassan *et al.*, [13] (0.030-100.00 µg/g). Iturbe *et al.*, [14] reported TPH up to 130000 mg/Kg and Torres *et al.*, [15] (51550 to 192130 mg/Kg) were far above this work.

According to DPR [16], the presence of petroleum hydrocarbon in soil at concentrations greater than 1000.00 mg/Kg is toxic to plants and animals that inhabit the soil. This effect in most cases are seen visibly, when the leaves of plants in petroleum contaminated areas turn brownish and withers off without passing through the drying process, but through decaying process. The health issues associated with TPH excessive intake in human body are headaches, dizziness nerve disorder (peripheral neuropathy), which is numbness in the feet and legs. Other effects of TPH compounds are on the blood, immune system, lungs, skin and eyes [17]. The observed high concentration of TPH in soils from the examined asphalt sites revealed that the soils from these areas are contaminated and so do not support

farming on such areas until proper soil remediation has been performed. Consequently, plants that might be found within the area is not advisable for both human and animal consumption since there is the possibility of toxicity resulting from eating of contaminated food, which may have taken-up TPH compounds from the soil.

Conclusion

This work showed that there was high level of total petroleum hydrocarbon in soil samples obtained from the three areas. Comparative analysis showed that the levels were higher than Department of Petroleum Resources set limit. It is therefore recommended that firm legislations and improvement on the existing environmental legislation be made to avert impending danger to human lives. The industries within the Niger Delta area, especially those around Port Harcourt metropolis must ensure that their effluent containing TPH compounds be carefully managed to minimize the pollution of environmental media. Thus, immediate remediation of the soil from these areas be conducted as soon as these companies vacate the area before farming on such lands be carried out.

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